

The 1986 Chemistry Articles
Most Cited 1986-1988, Plus 1989-1990 Data:
Catalysts, Clusters, Kinetics, and Theory

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Current Contents® has regularly identified and discussed papers in chemistry that become highly cited soon after their initial publication. The two most recent examples concerned 1984 chemistry papers most cited from 1984 to 1986¹ and 1985 chemistry articles most cited from 1985 to 1987.² This essay covers the 1986 chemistry articles most cited from 1986 to 1988. As before, this does not merely involve determining a suitable citation threshold for inclusion in this essay. An in-house subset of the *Science Citation Index*® known as the "Chemistry Citation Index" is used to limit the selection to chemistry. Nonetheless, the interdisciplinary nature of chemical research is still apparent. The journals publishing the largest number of highly cited

papers continue to include the *Journal of Chemical Physics* and the *Journal of Physical Chemistry* (see Table 1). The most-cited paper of all, "Enzymes in organic synthesis" by J. Bryan Jones, University of Toronto, Ontario, Canada, is also interdisciplinary but appeared in *Tetrahedron*.

The 101 papers listed below received a median of 42 citations and an average of 45.4 (4.4 citations in 1986, 18.4 in 1987, and 22.6 in 1988). The numbers ranged from a high of 99 to a low of 35 citations, the threshold value for inclusion. Not surprisingly, no fewer than 29 of the papers are review papers, including the two most cited. The second most-cited paper, by Roger Atkinson, University of California, Riverside, appeared in *Chemical Reviews*, which to-

Bibliography: The 1986 chemistry articles most cited in the SCI[®], 1986-1988. Articles are listed in alphabetic order by first author. Numbers following the bibliographic entry indicate the 1986, 1987, and 1988 SCI/SSCI[®] research-front specialties for which these are core papers. A=1986 citations. B=1987 citations. C=1988 citations. D=total 1986-1988 citations. E=1989 citations. F=1990 citations. G=total 1986-1990 citations.

A	B	C	D	E	F	G	Bibliographic Data
3	15	21	39	27	20	86	Alexakis A, Berlan J & Besace Y. Organocopper conjugate addition reaction in the presence of trimethylchlorosilane. <i>Tetrahedron Lett.</i> 27:1047-50, 1986. 88-0529
4	17	0	21	17	19	57	Andrieux C P, Gallardo I, Savéant J-M & Su K-B. Dissociative electron transfer. Homogeneous and heterogeneous reductive cleavage of the carbon-halogen bond in simple aliphatic halides. <i>J. Amer. Chem. Soc.</i> 108:638-47, 1986. 87-0366, 88-0451
9	33	46	88	39	53	180	Atkinson R. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. <i>Chem. Rev.</i> 86:69-201, 1986. 87-1336, 88-1401
1	16	18	35	21	30	86	Balasubramanian K. CAS SCF/CI calculations of low-lying states of SnH ₂ . <i>Chem. Phys. Lett.</i> 127:585-9, 1986. 87-1603
6	14	36	56	49	81	186	Bax A & Summers M F. ¹ H and ¹³ C assignments from sensitivity-enhanced detection of heteronuclear multiple-bond connectivity by 2D multiple quantum NMR. <i>J. Amer. Chem. Soc.</i> 108:2093-4, 1986. 88-2043
0	15	21	36	10	7	53	Binger P, Milczarek R, Mynott R, Regitz M & Rösch W. 1,3-diphosphacyclobutadienecobalt(I) complexes from phosphalkynes. <i>Angew. Chem. Int. Ed.</i> 25:644-5, 1986.
7	12	17	36	16	10	62	Boxer S G, Lockhart D J & Middendorf T R. Photochemical hole-burning in photosynthetic reaction centers. <i>Chem. Phys. Lett.</i> 123:476-82, 1986.
5	12	18	35	12	11	58	Breckenridge W H, Jouvét C & Soep B. Orbitally selective chemical reaction in Hg-H ₂ van der Waals complexes. <i>J. Chem. Phys.</i> 84:1443-50, 1986. 88-3141
14	13	23	50	21	16	87	Brucat P J, Zheng L S, Pettiette C L, Yang S & Smalley R E. Metal cluster ion photofragmentation. <i>J. Chem. Phys.</i> 84:3078-88, 1986.
8	20	16	44	22	11	77	Bruno J W, Smith G M, Marks T J, Fair C K, Schultz A J & Williams J M. C-H activation mechanisms and regioselectivity in the cyclometalation reactions of bis(pentamethylcyclopentadienyl)thorium dialkyl complexes. <i>J. Amer. Chem. Soc.</i> 108:40-56, 1986.
2	25	24	51	27	35	113	Brus L. Electronic wave functions in semiconductor clusters: experiment and theory. <i>J. Phys. Chem.</i> 90:2555-60, 1986. 87-3447, 88-1764
16	13	27	56	18	27	101	Buchanan J M, Stryker J M & Bergman R G. A structural, kinetic, and thermodynamic study of the reversible thermal C-H activation/reductive elimination of alkanes at iridium. <i>J. Amer. Chem. Soc.</i> 108:1537-50, 1986.
3	20	19	42	12	6	60	Burlingame A L, Baillie T A & Derrick P J. Mass spectrometry. <i>Anal. Chem.</i> 58:165R-211R, 1986. 87-0076, 88-3459
3	7	25	35	12	9	56	Butler L J, Tleich T M, Likar M D & Crim F F. Vibrational overtone spectroscopy of bound and predissociative states of hydrogen peroxide cooled in a supersonic expansion. <i>J. Chem. Phys.</i> 85:2331-2, 1986.
0	15	24	39	20	26	85	Castleman A W & Keesee R G. Ionic clusters. <i>Chem. Rev.</i> 86:589-618, 1986. 88-3391
0	26	36	52	36	49	137	Closs G L, Calcaterra L T, Green N J, Penfield K W & Miller J R. Distance, stereoelectronic effects, and the Marcus inverted region in intramolecular electron transfer in organic radical anions. <i>J. Phys. Chem.</i> 90:3673-83, 1986. 88-0270
1	17	24	42	24	14	80	Collman J P, Kodadek T & Brauman J I. Oxygenation of styrene by cytochrome P-450 model systems: a mechanistic study. <i>J. Amer. Chem. Soc.</i> 108:2588-94, 1986.
0	16	27	43	16	11	70	Colquhoun H M, Stoddart J F & Williams D J. Second-sphere coordination—a novel role for molecular receptors. <i>Angew. Chem. Int. Ed.</i> 25:487-582, 1986. 88-1213
10	17	12	39	12	9	60	Conrad E H, Aten R M, Kaufman D S, Allen L R, Engel T, den Nijs M & Riedel E K. Observation of surface roughening on Ni(115). <i>J. Chem. Phys.</i> 84:1015-28, 1986. 87-1410
0	17	25	42	27	10	79	Cook B R, Reinert T J & Suslick K S. Shape selective alkane hydroxylation by metalloporphyrin catalysts. <i>J. Amer. Chem. Soc.</i> 108:7281-6, 1986.
0	13	24	37	28	22	87	Covey T R, Lee E D, Bruins A P & Henlon J D. Liquid chromatography/mass spectrometry. <i>Anal. Chem.</i> 58:1451A-61A, 1986. 87-0449, 88-0086

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6	19	22	47	11	10	68	Crabtree R H & Hamilton D G. Classical (M = Os) and nonclassical (M = Fe, Ru) polyhydride structures for the complexes $MH_4(PR_3)_3$. <i>J. Amer. Chem. Soc.</i> 108:3124-5, 1986. 87-4349, 88-2569
2	30	36	68	26	25	119	Crabtree R H, Lavin M & Bonneviot L. Some molecular hydrogen complexes of iridium. <i>J. Amer. Chem. Soc.</i> 108:4032-7, 1986. 87-4349, 88-2569
0	13	53	66	32	41	139	Cram D J. Preorganization—from solvents to spherands. <i>Angew. Chem. Int. Ed.</i> 25:1039-57, 1986. 87-4492
0	11	25	36	19	36	91	Dance I G. The structural chemistry of metal thiolate complexes. <i>Polyhedron</i> 5:1037-104, 1986. 87-0193, 88-2803
2	17	18	37	20	14	71	Davis M J & Gray S K. Unimolecular reactions and phase space bottlenecks. <i>J. Chem. Phys.</i> 84:5389-411, 1986.
0	16	19	35	30	21	86	Dewar M J S, Olivella S & Stewart J J P. Mechanism of the Diels-Alder reaction: reactions of butadiene with ethylene and cyanoethylenes. <i>J. Amer. Chem. Soc.</i> 108:5771-9, 1986. 87-3372, 88-0710
9	24	14	47	4	6	57	Disch R L & Schulman J M. On symmetrical clusters of carbon atoms: C_{60} . <i>Chem. Phys. Lett.</i> 125:465-6, 1986.
7	36	32	75	23	41	139	Frisch M J, Del Bene J E, Binkley J S & Schaefer H F. Extensive theoretical studies of the hydrogen-bonded complexes $(H_2O)_2$, $(H_2O)_2H^+$, $(HF)_2$, $(HF)_2H^+$, F_2H^+ , and $(NH_3)_2$. <i>J. Chem. Phys.</i> 84:2279-89, 1986. 87-3111, 88-30490
0	14	32	46	16	19	81	Gericke K-H, Klee S, Comes F J & Dixon R N. Dynamics of H_2O_2 photodissociation: OH product state and momentum distribution characterized by sub-Doppler and polarization spectroscopy. <i>J. Chem. Phys.</i> 85:4463-79, 1986. 88-0725
14	15	14	43	4	5	52	Geusic M E, McIlrath T J, Jarrold M F, Bloomfield L A, Freeman R R & Brown W L. Photofragmentation of mass-resolved carbon cluster ions: observation of a magic neutral fragment. <i>J. Chem. Phys.</i> 84:2421-2, 1986.
0	16	19	35	26	12	73	Gilliom L R & Grubbs R H. Titanacyclobutanes derived from strained cyclic olefins: the living polymerization of norbornene. <i>J. Amer. Chem. Soc.</i> 108:733-42, 1986. 87-0121, 88-0838
5	20	21	46	23	20	89	Groves J T & Watanabe Y. On the mechanism of olefin epoxidation by oxo-iron porphyrins. Direct observation of an intermediate. <i>J. Amer. Chem. Soc.</i> 108:507-8, 1986.
2	14	20	36	21	11	68	Guthrie E J & Schwartz H E. Integral pressure restrictor for capillary SFC. <i>J. Chromatogr. Sci.</i> 24:236-41, 1986. 88-2808
4	21	12	37	9	11	57	Gutowski M, Van Lenthe J H, Verbeek J, Van Duijneveldt F B & Chataśński G. The basis set superposition error in correlated electronic structure calculations. <i>Chem. Phys. Lett.</i> 124:370-5, 1986.
10	25	14	49	5	10	64	Haddon R C, Brus L E & Raghavachari K. Electronic structure and bonding in icosahedral C_{60} . <i>Chem. Phys. Lett.</i> 125:459-64, 1986.
9	26	19	54	26	21	101	Hanson R M & Sharpless K B. Procedure for the catalytic asymmetric epoxidation of allylic alcohols in the presence of molecular sieves. <i>J. Org. Chem.</i> 51:1922-5, 1986. 87-0802, 88-2195
12	22	19	53	7	7	67	Haymet A D J. Footballene: a theoretical prediction for the stable, truncated icosahedral molecule C_{60} . <i>J. Amer. Chem. Soc.</i> 108:319-21, 1986. 87-1267
5	21	18	44	5	9	58	Haymet A D J & Oxtoby D W. A molecular theory for freezing: comparison of theories, and results for hard spheres. <i>J. Chem. Phys.</i> 84:1769-77, 1986. 87-4581
13	35	29	77	17	22	116	Herrmann W A. Multiple bonds between transition metals and "bare" main group elements: links between solid state chemistry and organometallic chemistry. <i>Angew. Chem. Int. Ed.</i> 25:56-76, 1986. 87-6624
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0	14	25	39	30	27	96	Hess B A, Schaad L J, Čársky P & Zahradník R. Ab initio calculations of vibrational spectra and their use in the identification of unusual molecules. <i>Chem. Rev.</i> 86:709-30, 1986. 88-1623
3	18	22	43	13	13	69	Hills M M, Parmeter J E, Mullins C B & Weinberg W H. Interaction of ethylene with the Ru(001) surface. <i>J. Amer. Chem. Soc.</i> 108:3554-62, 1986.
1	13	22	36	24	15	75	Horiguchi Y, Matsuzawa S, Nakamura E & Kuwajima I. $Me_3SiCl/HMPA$ accelerated conjugate addition of copper reagent. Stereoselective synthesis of enol silyl ether of aldehyde. <i>Tetrahedron Lett.</i> 27:4025-8, 1986. 87-0305, 88-0529

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3	30	29	62	24	29	115	Houk R S. Mass spectrometry of inductively coupled plasmas. <i>Anal. Chem.</i> 58:97A-105A, 1986. 87-1442, 88-0965
0	12	28	40	28	9	77	Huang Z S, Jucks K W & Miller R E. The vibrational predissociation lifetime of the HF dimer upon exciting the "free-H" stretching vibration. <i>J. Chem. Phys.</i> 85:3338-41, 1986.
2	21	13	36	11	8	55	Hurst G J B, Fowler P W, Stone A J & Buckingham A D. Intermolecular forces in van der Waals dimers. <i>Int. J. Quantum Chem.</i> 29:1223-39, 1986.
1	15	25	41	31	31	103	Hynes J T. Outer-sphere electron-transfer reactions and frequency-dependent friction. <i>J. Phys. Chem.</i> 90:3701-6, 1986.
8	17	18	43	9	11	63	Jasinski J M. Absolute rate constant for the reactions SiH ₂ + D ₂ . <i>J. Phys. Chem.</i> 90:555-7, 1986.
3	16	18	37	23	22	82	Jellinek J, Beck T L & Berry R S. Solid-liquid phase changes in simulated isoenergetic Ar ₁₃ . <i>J. Chem. Phys.</i> 84:2783-94, 1986.
5	16	18	36	13	5	54	Jonah C D, Romero C & Rahman A. Hydrated electron revisited via the Feynman path integral route. <i>Chem. Phys. Lett.</i> 123:209-14, 1986.
4	39	56	99	70	68	237	Jones J B. Enzymes in organic synthesis. <i>Tetrahedron</i> 42:3351-3403, 1986. 87-7011, 88-2696
15	27	18	60	33	28	121	Jurczak J, Pikul S & Bauer T. (R)- and (S)-2,3-O-isopropylidene-glyceraldehyde in stereoselective organic synthesis. <i>Tetrahedron</i> 42:447-88, 1986. 86-0989, 87-1842, 88-1564
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0	17	29	46	33	33	112	Keese R G & Castleman A W. Thermochemical data on gas-phase ion-molecule association and clustering reactions. <i>J. Phys. Chem. Ref. Data</i> 15:1011-71, 1986. 87-7119
11	28	20	59	11	11	81	Klein D J, Schmalz T G, Hite G E & Seltz W A. Resonance in C ₆₀ buckminsterfullerene. <i>J. Amer. Chem. Soc.</i> 108:1301-2, 1986. 87-1267, 88-1654
4	21	16	41	12	10	63	Klein J. Dynamics of entangled linear, branched, and cyclic polymers. <i>Macromolecules</i> 19:105-18, 1986.
4	20	17	41	21	14	76	Kochi J K. Electron transfer and transient radicals in organometallic chemistry. <i>J. Organometal. Chem.</i> 300:139-66, 1986.
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2	21	34	57	35	38	130	Koutecký J & Fantucci P. Theoretical aspects of metal atom clusters. <i>Chem. Rev.</i> 86:539-87, 1986.
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2	16	18	36	23	25	84	Kuppermann A & Hipes P G. Three-dimensional quantum mechanical reactive scattering using symmetrized hyperspherical coordinates. <i>J. Chem. Phys.</i> 84:5962-4, 1986.
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0	19	29	48	19	26	93	Legon A C & Millen D J. Gas-phase spectroscopy and the properties of hydrogen-bonded dimers: HCN...HF as the spectroscopic prototype. <i>Chem. Rev.</i> 86:635-57, 1986. 88-1700
4	16	15	35	16	13	64	Lin C-H, Campbell K D, Wang J-X & Lunsford J H. Oxidative dimerization of methane over lanthanum oxide. <i>J. Phys. Chem.</i> 90:534-7, 1986.
4	12	28	44	19	25	88	Low J J & Goddard W A. Theoretical studies of oxidative addition and reductive elimination. 2. Reductive coupling of H-H, H-C, and C-C bonds from palladium and platinum complexes. <i>Organometallics</i> 5:609-22, 1986.
8	19	21	48	12	9	69	Luke B T, Pople J A, Krogh-Jespersen M-B, Apeloig Y, Chandrasekhar J & Schleyer P v R. A theoretical survey of singly bonded silicon compounds. Comparison of the structures and bond energies of silyl and methyl derivatives. <i>J. Amer. Chem. Soc.</i> 108:260-9, 1986.

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0	13	36	49	63	62	174	Morse M D. Clusters of transition-metal atoms. <i>Chem. Rev.</i> 86:1049-109, 1986. 88-1654
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6	21	15	42	8	8	58	Newton M D & Stanton R E. Stability of buckminsterfullerene and related carbon clusters. <i>J. Amer. Chem. Soc.</i> 108:2469-70, 1986.
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4	14	19	37	23	28	88	Raghavachari K. Theoretical study of small silicon clusters: equilibrium geometries and electronic structures of Si _n (n=2-7,10). <i>J. Chem. Phys.</i> 84:5672-86, 1986.
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12	10	14	36	8	8	52	Scherer O J, Schwalb J, Wolmershäuser G, Kaim W & Gross R. <i>cyclo-P₅</i> as complex ligand—the phosphorus analogue of the cyclopentadienyl ligand. <i>Angew. Chem. Int. Ed.</i> 25:363-4, 1986.
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3	15	23	41	13	16	70	Widom B. Lattice model of microemulsions. <i>J. Chem. Phys.</i> 84:6943-54, 1986. 87-0095, 88-1249
14	18	20	52	18	20	90	Yamaguchi Y, Frisch M, Gaw J, Schaefer H F & Binkley J S. Analytic evaluation and basis set dependence of intensities of infrared spectra. <i>J. Chem. Phys.</i> 84:2262-78, 1986.
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gether with *Angewandte Chemie International Edition* is particularly well represented (8 out of 101 papers each in this database). Review journals traditionally have shown the highest citation impact.

Research Fronts

Enzymes and Other Catalysts

The Jones paper, mentioned above, was published as *Tetrahedron Report* (#203). Enzymes have been extensively used in the pharmaceutical industry to promote synthetic changes in organic molecules, especially to act as specific and chiral catalysts. They now see more routine use in biochemical and synthetic organic chemical work. This extensive review (54 pages, 388 references) covers the literature of 1984. The emphasis is on readily available enzymes, such as from baker's yeast. The paper stresses experimental aspects of enzymic reactions.

The review is subdivided into sections about exploiting structural specificity for se-

lective reactions, enantiomeric specificity, prochiral stereospecificity, and combinations of enzyme specificity, multiple enzyme reactions, stereospecific introduction of isotope labels, and a prognosis for the future. The scope of the review is enormous, as there exists an enzyme-catalyzed equivalent to most organic reactions and more than 2,000 known enzymes. Aside from their selectivity, the major advantage of enzymic reactions is that they take place under mild conditions (room temperature, neutral pH), which minimizes many potential problems, such as rearrangement, within the organic synthesis.

Although this is the only paper listed on enzyme-mediated synthesis, there are a number of papers on other types of catalytic reactions. Transition metal complexes of small, neutral molecules drew significant interest. Metal hydrogen complexes were the most investigated, including those of mercury (W.H. Breckenridge, Christophe Jouvét, and Benoit Soep, University of Paris-South, Orsay), iridium (see below), molybdenum and tungsten (Gregory J.

Kubas, and colleagues, Los Alamos National Laboratory, New Mexico), and palladium and platinum (John J. Low and William A. Goddard, California Institute of Technology [Caltech], Pasadena).

One such paper is entitled "Some molecular hydrogen complexes of iridium," by Robert H. Crabtree, Maryellen Lavin, and L. Bonneviot, Yale University. This *JACS* paper describes the new molecular hydrogen complexes $[\text{IrH}(\text{H}_2)(\text{bq})\text{L}_2]^+$ and $[\text{IrH}_2(\text{H}_2)(\text{PCy}_3)_2]^+$ ($\text{bq}=7,8\text{-benzoquinolate}$, $\text{L}=\text{PPh}_3$ or PCy_3), and their detection via $^1\text{H-NMR}$ T_1 studies. The catalysts are generated through the reaction of molecular hydrogen with the aquo complex, which is in turn obtained through the reaction of $[\text{Ir}(\text{cod})\text{L}_2]\text{SbF}_6$ in moist methylene chloride at 0°C under hydrogen. The uptake of molecular hydrogen is reversible, as passing nitrogen gas through the solution rapidly reforms the aquo complex.

The H-H bond is more easily broken in the coordinated complex, as a result of the donation from the bond to the metal. This is similar to the activation of C-H bonds by metal centers (see below). The mechanism of the coordinated H_2 being deprotonated, forming the neutral dihydride, is elegantly shown by isotopically substituting both the hydridic and dihydrogen sites. In the T_1 studies (inversion recovery), the dihydrogen protons relax much faster than the terminal hydride, and are thus detectable. The authors conclude that it is likely that many other such dihydride complexes are unrecognized in the literature, suggesting that a re-examination of such materials is in order.

This area has appeared in lists of highly cited papers several times before. The binding of molecular hydrogen to metals was unknown until 1984, when Kubas and his colleagues at Los Alamos characterized the complex $[\text{W}(\text{H}_2)(\text{CO})_3(\text{PR}_3)_2]$.³ The original reference appeared on the 1984 most-cited chemistry list,¹ and other complexes have been characterized by the same group.⁴ Several papers on this subject appeared on the 1985 list as well.⁵⁻⁸

Crabtree's work in the closely related area of C-H bond activation was on our 1985 list.

Table 1: The 21 journals that published the papers listed in the Bibliography. The numbers in parentheses are the 1986 impact factors for the journals. (The 1986 impact factor equals the number of 1986 citations received by the 1984-1985 articles in a journal divided by the number of articles published by the journal during that same period.) Data were taken from the 1986 *JCR*®. The figures at the right indicate how many papers from each journal appear in the Bibliography.

Journal	Number of Papers
J. Chem. Phys. (3.300)	27
J. Amer. Chem. Soc. (4.435)	20
J. Phys. Chem. (2.967)	9
*Angew. Chem. Int. Ed. (5.335)	8
Chem. Rev. (7.400)	8
Chem. Phys. Lett. (2.226)	7
Anal. Chem. (3.797)	4
J. Organometal. Chem. (1.179)	3
Tetrahedron (2.031)	2
Tetrahedron Lett. (2.158)	2
Annu. Rev. Phys. Chem. (7.159)	1
Catal. Rev.-Sci. Eng. (2.429)	1
Int. J. Quantum Chem. (1.173)	1
J. Catal. (2.527)	1
J. Chem. Soc. Chem. Commun. (2.385)	1
J. Chromatogr. Sci. (2.415)	1
J. Org. Chem. (2.079)	1
J. Phys. Chem. Ref. Data (N/A)	1
Macromolecules (2.227)	1
Organometallics (3.588)	1
Polyhedron (1.154)	1

*Also published in German as *Angew. Chem.*

That review paper covered "The organometallic chemistry of alkanes,"⁹ and was one of the core papers on "Arene C-H bond activation, molecular hydrogen complexes, catalytic intermolecular h/d exchange, and aliphatic C-H bonds" (#86-3302). An additional paper on "C-H and H-H bond activation: dissociative vs. nondissociative binding to iridium"¹⁰ is clearly a precursor to the 1986 work.

Activation of organic ligands by transition metals continues to be heavily studied, including the cyclometalation reactions of thorium dialkyl complexes (Joseph W. Bruno, Northwestern University, Evanston, Illinois, and colleagues), shape selective hydroxylation of alkanes by metalloporphyrin catalysis (Bruce R. Cook, Thomas J. Reinert, and Kenneth S. Suslick, University of Illinois, Urbana Champaign), epoxidation of olefins by oxo-iron porphyrins (John T. Groves and Yoshito Watanabe, University of Michigan, Ann Arbor), physical studies

of ethylene on the ruthenium (001) surface (M.M. Hills and colleagues, Caltech) chemisorption of methane on Ni(111) (M.B. Lee and colleagues, MIT), oxidative dimerization of methane over lanthanum oxide (Chiu-Hsun Lin and colleagues, Texas A&M, College Station), and the synthesis of ethylene and ethane via oxidative coupling of methane (Kiyoshi Otsuka and colleagues, Tokyo Institute of Technology, Japan).

Cluster Chemistry

Several research areas continued to be active in 1986—the most notable being cluster chemistry. Metal clusters have long been studied as models for metal catalysts. Several papers were in the area of transition metal clusters, including metal cluster ion photofragmentation (P.J. Brucat and colleagues, Rice University, Houston, Texas), electronic structure effects in metal clusters (Manfred M. Kappes and coworkers, University of Bern, Switzerland), theoretical aspects of metal atom clusters (Jaroslav Koutecký, Free University of Berlin, Federal Republic of Germany (FRG), and Piercarlo Fantucci, University of Milan, Italy), electron binding and chemical inertness of niobium clusters (R.L. Whetten and colleagues, Exxon Research and Engineering Company, Annandale, New Jersey), and a review paper on the clusters of transition-metal atoms (Michael D. Morse, University of Utah, Salt Lake City). An additional review paper appeared on the subject of ionic clusters (A.W. Castleman and R.G. Keesee, Pennsylvania State University, University Park).

Smaller clusters also were covered in a review paper dealing with the bonding, kinetics, and approach to equilibrium structures of simple metallic, molecular, and network microclusters (J.C. Phillips, AT&T Bell Labs, Murray Hill, New Jersey), as was an additional equilibrium structure theoretical study (Krishnan Raghavachari, AT&T Bell Labs). Finally, electronic wave functions were studied for semiconductor clusters (Louis Brus, AT&T Bell Labs). Several papers on this topic also appeared in the

1985 list, including two by the Exxon group mentioned above^{11,12} and Morse.¹³

Buckminsterfullerene Carbon Cluster

In the "organic" area, seven papers dealt with carbon clusters, with C₆₀ clusters being the primary focus. The 1985 literature review described in detail the interest in the hollow molecule "buckminsterfullerene," which clearly continues to the present day.² This work formed the core of two research fronts: #87-1267, "Carbon clusters, icosahedral C₆₀, and vanishingly small ring current magnetic-susceptibility" ("Footballene: a theoretical prediction for the stable, truncated icosahedral molecule C₆₀" by A.D.J. Haymet, University of California, Berkeley (UCB), and Q.L. Zhang and colleagues, Rice University, discussed in detail below), and #88-1654, "Carbon cluster ions, potential-energy surfaces, and icosahedral gold small particles" ("Resonance in C₆₀, buckminsterfullerene," by D.J. Klein and colleagues, Texas A&M, Galveston, and "Clusters of transition metal atoms," by Morse, mentioned earlier). The other papers focusing on buckminsterfullerene and other such clusters discussed their photofragmentation, their electronic structure and bonding, and their stability.

Soot: Q.L. Zhang's Group

Aside from their aesthetic and catalytic appeal, large carbon clusters are thought to be key intermediates in the formation and morphology of soot, the subject of the paper by Zhang et al., published in the *Journal of Physical Chemistry*. An earlier paper¹⁴ on this subject, by H.W. Kroto and colleagues, was the second most-cited paper in the 1985 list² and is one of the core papers on "Small alkali metal clusters, metal cluster ion photofragmentation, Fourier transform ion cyclotron resonance mass spectrometry, and magic number" (#86-2748). The Rice University group proposes that the stability of the C₆₀ cluster arises from the ability of small sections of the graphite sheet (from which the buckminsterfullerene is prepared

by vaporization) to close into spheroidal shells, thereby eliminating any reactive edges.

All clusters containing even numbers of carbon atoms in the 40-80 carbon range, in fact, were found to be resistant to chemical attack. This is attributed to the possibility of forming closed shells by using a combination of 12 pentagons and $(n/2)-10$ hexagons (n =number of carbons). Odd clusters cannot form such closed shells, and are quite reactive. This reactivity, and the propensity to form closed shells offers a possible mechanism for soot formation: the reactive odd clusters try to form closed shells, but because of the abundance of hydrogen in the flame, etc., the carbon net is likely to close imperfectly, resulting in a second shell beginning before the first has been completed. The overall result is a soot nucleus consisting of concentric, but imperfect, spheres, which presents an active front for further growth. Earlier work investigated inorganic aspects using the C_{60} and smaller clusters as complex ligands, similar to benzene and cyclopentadiene, in the area of main group and lanthanide chemistry.¹⁵

Hydroxyl Radical: R. Atkinson

As noted earlier, the *Chemical Reviews* paper detailing the "Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions," by Atkinson, was the second most-cited paper. The hydroxyl (OH) radical plays an important role in combustion and atmospheric chemistry, serving as the dominant species in the degradation of organic compounds. Thus, the kinetics and mechanism of OH radical reactions have been the focus of a large number of investigations. This extensive review (132 pages, 550 references) covers those mechanisms that occur at temperatures below 500K.

Hydrogen-Bonded Complexes

One of the highly cited papers is in the area of theoretical chemistry, entitled "Ex-

tensive theoretical studies of the hydrogen-bonded complexes $(H_2O)_2$, $(H_2O)_2H^+$, $(HF)_2$, $(HF)_2H^+$, F_2H^+ , and $(NH_3)_2$," by Michael J. Frisch, UCB, Janet E. Del Bene, Youngstown State University, Ohio, J. Stephen Binkley, Sandia National Laboratories, Livermore, California, and Henry F. Schaefer, University of Georgia, Atlanta. Published in the *Journal of Chemical Physics*, this study examines the above-mentioned molecules using large basis sets and optimization of structures, including the effects of electron correlation. Single bond energies of excellent accuracy are obtained in this manner (usually +2 kcal/mol). Comparisons of previous theoretical studies with experimental data are made. Frisch coauthored a paper with Del Bene and J.A. Pople, Carnegie-Mellon University, Pittsburgh, Pennsylvania, on this subject in the 1985 list, entitled "Molecular orbital study of the dimers $(AH)_2$ formed from NH_3 , OH_2 , FH , PH_3 , SH_2 , and ClH ."¹⁶

Electron Transfer Reactions, Silicon Chemistry, and Other Research Fronts

Other significant research areas included electron transfer reactions and silicon chemistry. The broadest research front in 1987-1988 (Table 2) centered on "*Ab initio* calculation, C-H bond, and formation for 2nd-row hydrides" (#88-1623). Of 56 core papers for this front, only two papers were from this 1986 list (B. Andes Hess, Vanderbilt University, Nashville, and colleagues, and N. Bernhard Schlegel, Wayne State University, Detroit). However, there were 1,057 citing (published) papers in 1988 alone. It also is tied to the more general area of C-H bond activation by transition metals, discussed earlier.

The second largest front (#88-0270), with 726 published papers in 1988, dealt with "Intramolecular electron-transfer, solvation dynamics, solvent saturation and dioxygen copper reactivity." Of 50 core papers, two were from this list (G.L. Closs et al., University of Chicago, and Edward M. Kosower and Dan Huppert, Tel-Aviv Uni-

Table 2: The 1967 and 1988 ISI® research fronts that include at least two of the most-cited 1986 chemistry papers as core documents. A=number of Bibliography papers that are core to each research front. B=total number of core documents. C=total number of citing papers published for the year designated by the prefix.

Number	Name	A	B	C
87-1267	Carbon clusters, icosahedral C ₆₀ , and vanishingly small ring current magnetic-susceptibility	3	16	189
87-1442	Inductively coupled plasma mass-spectrometry, boron isotope ratios in geological materials, and easily ionizable concomitant elements	2	22	131
87-3077	Oxidative coupling of methane, oxide catalysts, and highly selective ethane formation	2	20	122
87-3447	Colloidal semiconductor particles, size quantization, and illuminated CdS	3	21	195
87-4349	Molecular-hydrogen complexes, dihydrogen coordination, methane activation, and dinitrogen ligands	3	7	99
88-0270	Intramolecular electron-transfer, solvation dynamics, solvent saturation, and dioxygen copper reactivity	2	50	726
88-0367	Oxidative coupling of methane, CO + NO, and RB+ doped MGO catalysts	2	43	361
88-0529	Functionalized organocopper reagents, allylic stereocenter directed asymmetric conjugate addition, organocuprate reactivity selectivity, and copper chemistry	2	21	169
88-1623	<i>Ab initio</i> calculation, C-H bond, and formation for second-row hydrides	2	56	1,057
88-1654	Carbon cluster ions, potential-energy surfaces, and icosahedral gold small particles	18	3	240
88-2569	Molecular-hydrogen complexes, reversible protonation of iron dihydrides, oligophosphane ligands, and η ² -H ₂ for R	3	9	128

versity, Israel). But, as mentioned previously, three of these papers dealt with electron transfer.

Other fronts appearing in the 1985 report that remain active include: #87-1442, "Inductively coupled plasma mass-spectrometry, boron isotope ratios in geological materials, and easily ionizable concomitant elements," and #87-3077, "Oxidative coupling of methane, oxide catalysts, and highly selective ethane formation." Work in this area was mentioned above as part of the general research in activation of organic ligands by transition metals.

Many research fronts experienced declines in interest, as they matured and broadened out. Nuclear magnetic resonance (NMR) was the dominant research front in 1983¹⁷ and in 1985.² However, it all but disappeared from the 1986 list, with only one paper (Ad Bax, National Institutes of Health, and Michael F. Summers, Food and Drug Administration, Bethesda, Maryland) on the subject. And the research front on superconductivity disappeared altogether.

Authors

A grand total of 293 authors were represented on the 1986 list of most-cited papers. The majority, 269, were authors on single papers, while 23 were associated with two papers. Schaefer was the most prolific, co-

authoring three papers (see papers by Frisch, Rice, and Yamaguchi). As noted in Table 3, the number of authors per paper ranged from one to nine. The mean was just under three (2.9). One Nobel laureate appeared on the list, Donald J. Cram, University of California, Los Angeles (chemistry, 1987).¹⁸ Many of the authors were also represented on the 1984 and 1985 lists, indicating the continuing interest in their research.

Universities and research institutes from many nations were represented (Table 4). The largest number (77) of authors continued to be from the US, followed by the FRG (8), the UK (5), and Israel and Japan (4 each). International coauthorship was widespread, accounting for more than 10 percent of the papers. The most prolific institutions were Caltech (8 papers) and UCB (6). In addition, AT&T Bell Laboratories, Argonne

Table 3: The number of authors per paper for the 1986 chemistry articles most cited in the SCI®, 1986-1988.

Number of Authors per Paper	Number of Papers
9	1
7	2
6	5
5	10
4	17
3	19
2	24
1	23

National Laboratory, Illinois and the University of Wisconsin, Madison, each published five papers.

Conclusions

Several trends seen in earlier studies continue here. The top three journals remain the same, although their order has changed. For the first time, the *Journal of the American Chemical Society* did not publish the largest number of most-cited papers, dropping to second with 20 (Table 1). Chemical physics and physical chemistry journals dominate, including the *Journal of Chemical Physics* (1st, 27 papers), the *Journal of Physical Chemistry* (3rd, 9 papers) and, *Chemical Physics Letters* (5th, 7 papers). An additional four papers appear in other physical chemistry journals. Only two review journals turned up—*Chemical Reviews* and *Annual Review of Physical Chemistry*. One notable change is the absence of *Accounts of Chemical Research* (4th on the 1985 list).

As has been the case in the past, the overwhelming majority of highly cited papers were published in English—the sole exception was a paper in German on a “Chance discovery in the case of rhenium: oxo-complexes in high and low oxidation states,” by Wolfgang A. Herrmann, University of Munich, FRG, in the *Journal of Organometallic Chemistry*. It has been noted here in the past that publication of a paper in a language other than English usually guarantees a lower impact.¹⁹ However, Herrmann also published another paper on the list in English. An additional eight papers were pub-

Table 4: National locations of the institutional affiliations listed by authors in the Bibliography, according to total papers (column A). B=number of papers co-authored with researchers affiliated with institutions in other countries. C=national locations of institutions listed by coauthors.

Country	A	B	C
US	77	9	Australia, Czechoslovakia, FRG, Israel, Spain, UK, Yugoslavia
FRG	8	6	Israel, Italy, UK, US
UK	5	2	FRG, US
Israel	4	4	FRG, US
Japan	4	0	
Australia	2	1	US
France	2	0	
Poland	2	1	The Netherlands
Canada	1	0	
Czechoslovakia	1	1	US
GDR	1	0	
Italy	1	1	FRG
The Netherlands	1	1	Poland
Spain	1	1	US
Switzerland	1	0	
Yugoslavia	1	1	US

lished in German but also appeared in English translation (*Angewandte Chemie International Edition*).

The closely related areas of catalysis and cluster chemistry (both transition metal and carbon) dominate the list. This is reinforced by the largest of the research fronts, dealing with theoretical calculations of C-H bond strengths in second-row metal hydrides. However, NMR and superconductivity disappeared from this year's list. This does not mean a lack of interest in these areas, merely that no paper published in 1986 received the threshold level of citations. Earlier papers in these areas continued to be heavily cited.

Note from Eugene Garfield

Since the publication of this analysis was delayed by a year, there was the additional benefit of learning how many of these papers continued to be utilized in 1989 and 1990. The addition of these data demonstrate that work in chemistry usually requires a much longer period of time to demonstrate its impact. Consider especially the papers by Atkinson, Bax, Brus, Closs, Dance, Frisch, Hess, Hynes, Jones, Jurczak, Kavarnos, Koutecký, Morse, Sato, Stille, Sumi, and West. The paper by J.B. Jones appears to be well on its way to *Citation Classic*® status. And, not surprisingly, the subject of enzymes in organic synthesis has become a very hot area of chemistry, as implied in the opening of this essay. The Jones paper is the most-cited core paper in research front — #89-0501, Lipase catalyzed transesterifications in organic-solvents, enzymatic catalysis, immobilized enzymes, and enantiomeric purity—well ahead of the number two core paper by G.M. Whitesides that was one of the 100 most-cited 1985 chemistry papers from my earlier essay.²

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