measures of substituent effects in this regard.

Log k_0, where k_0 is the rate constant in the absence of surfactant, is well correlated by the polar substituent parameter[12] σ^0 (different from the ordinary Hammett σ in that σ^0 is derived for use with systems in which a saturated group is interposed between the benzene ring and the reaction center). A least-squares fit yields $\rho = -0.175$ with correlation coefficient 0.9820 and F test[11] 1%. This correlation is expected on the basis of earlier results.[13,14]

Log k_m, where k_m is the rate constant for reaction within the micelle, is not correlated by σ^0 and is only roughly correlated by π.

Experimental Section

Phenylacetohydroxamic acid and sodium dodecylsulfate have been described previously.[2] The substituted phenylacetohydroxamic acids were prepared according to the general procedure[14] described before. The IR and ^{1}H NMR spectra are consistent with the indicated structures. The acids were crystallized from water or aqueous ethanol. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. *p*-Methylacetohydroxamic acid, mp 158–159 °C. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 64.87; H, 6.85; N, 8.30. *m*-Methylphenylacetohydroxamic acid, mp 127–128 °C. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.58; H, 6.87; N, 8.37. *p*-Ethylphenylacetohydroxamic acid, mp 164–165 °C. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.01; H, 7.31; N, 7.82. Found: C, 67.21; H, 7.41; N, 7.82. *p*-Bromophenylacetohydroxamic acid, mp 157–158 °C. Anal. Calcd for $C_8H_8BrNO_2$: C, 41.76; H, 3.51; N, 6.09. Found: C, 41.67; H, 3.76; N, 5.79.

Sodium 1-dodecanesulfonate was prepared by reflux of aqueous sodium sulfite with 1-bromododecane.[15] It was purified by two extractions with hot petroleum ether, crystallization from methanol, followed by two recrystallizations from 95% ethanol. IR and ^{1}H NMR spectra of the surfactant were the same as published spectra.[16] Anal. Calcd for $C_{12}H_{25}SO_3Na$: C, 52.91; H, 9.25; S, 11.77. Found: C, 52.91; H, 9.26; S, 11.89.

The kinetic measurements were obtained by the method used previously.[2]

Registry No.—Sodium dodecylsulfate, 151-21-3; sodium 1-dodecanesulfonate, 2386-53-0.

References and Notes

(1) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, N.Y., 1975.
(2) D. C. Berndt and L. E. Sendelbach, *J. Org. Chem.*, **42**, 3305 (1977).
(3) V. Gani, C. Lapinte, and P. Viout, *Tetrahedron Lett.*, 4435 (1973).
(4) Reference 1, Chapter 4.
(5) J. Baumrucker, M. Calzadilla, and E. H. Cordes in "Reaction Kinetics in Micelles", E. H. Cordes, Ed., Plenum Press, New York, N.Y., 1973, Chapter 2.
(6) C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitani, and E. J. Lien, *J. Med. Chem.*, **16**, 1207 (1973).
(7) K. Meguro, T. Kondo, N. Ohba, T. Ino, and O. Yoda, *Bull. Chem. Soc. Jpn.*, **30**, 760 (1957).
(8) K. A. Wright, A. D. Abbott, V. Sivertz, and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 549 (1939).
(9) C. A. Bunton, *Tech. Chem. (N.Y.)*, **10**, 731 (1976).
(10) C. A. Bunton, K. Ohmenzetter, and L. Sepulveda, *J. Phys. Chem.*, **81**, 2000 (1977).
(11) D. A. Leabo, "Basic Statistics", 4th ed., Richard D. Irwin, Inc., Homewood, Ill., 1972, Chapter 16.
(12) O. Exner in "Advances in Linear Free Energy Relationships", J. Shorter and N. B. Chapman, Eds., Plenum Press, New York, N.Y., 1972, Chapter 2.
(13) D. C. Berndt and I. E. Ward, *J. Org. Chem.*, **43**, 13 (1978).
(14) D. C. Berndt and I. E. Ward, *J. Org. Chem.*, **39**, 841 (1974).
(15) H. V. Tartar and A. L. M. LeLong, *J. Phys. Chem.*, **59**, 1185 (1955).
(16) "Sadtler Standard Spectra", Sadtler Research Laboratories, Inc., Philadelphia, Pa.

Notes

Photochemical Oxidation of Alcohols by Fe^{3+}, Cu^{2+}, and Ag^{+} Ions. 2[1]

S. Rajan* and D. Ramesh[2]

Department of Chemistry, Vivekananda College, Madras 600 004, India

Received July 11, 1978

Very recently Stenberg[3] reported the photochemical oxidation of aliphatic alcohols by $FeCl_3$. Similar oxidation reactions are also known with ferric perchlorate.[4] We report here, for the first time, that Ag^+ and Cu^{2+} ions can photochemically oxidize alcohols and that these ions are better oxidizing agents than the reported Fe^{3+} ions. We have successfully oxidized aliphatic and aromatic alcohols, cyclic alcohols, and terpene alcohols with these metal ions in very high yields. $K_3Fe(CN)_6$ also oxidizes these alcohols. The reactions with Ag^+ ions are very clean, fast, and convenient for workup. Table I gives the results.

The irradiations were carried out in a Rayonet photochemical reactor using 350-nm lamps under a nitrogen atmosphere in Me_2SO–water mixture. The oxidation does not proceed in the presence of air. Reactions do not proceed in the dark. The isolated yields of the products range from 78–96%. The products are identified as the corresponding 2,4-dinitrophenyl hydrazone derivatives and are characterized in comparison with the reported melting point. The solvent Me_2SO by itself does not oxidize the alcohols and also does not get itself oxidized. The completion of the reaction in the case of $K_3Fe(CN)_6$ was marked by the formation of an intense blue precipitate (Turnbull's blue) by adding $FeCl_3$; in the case of reactions with Ag^+ ions by the total precipitation of Ag^0 and in the case of Cu^{2+} ions by the formation of a white precipitate. The nature of this white precipitate is not known. However, further studies are planned to determine it. In all these reactions, the completion was also checked by the absence of alcohols in IR and GLC. Stenberg[3] reports a minimum of 5 h of irradiation with $FeCl_3$ whereas Table I shows that even lesser times of exposure to light are sufficient for the total oxidation of alcohols.

Earlier reports of Brealey[5,6] and the recent report of Stenberg[3] both suggest ketyl radicals as intermediates in the photochemical oxidation of alcohols. As our reactions exhibit radical characteristics such as inhibition by oxygen, possibly similar ketyl radicals are involved in these reactions as well. We have questioned ourselves the nature of the excitation process in the Ag^+, Cu^{2+}, and Fe^{3+} ions and the species of photoexcitation, viz., inorganic cation, ion pair, or alcohol–salt complex. We do have some interesting preliminary results to these questions. However, our studies are still in progress and

---

* Address correspondence to this author at Greaves Foseco Ltd., Chinchwad, Poona-411 019, India.

0022-3263/79/1944-0138$01.00/0

Table I. Photochemical Oxidation of Alcohols by $K_3Fe(CN)_6$, $AgNO_3$, and $CuSO_4$[a]

No.	alcohol[b]	registry no.	oxidant	registry no.	time of irradiation, h	products[c]
1	isopropyl alcohol[d]	67-63-0	$K_3Fe(CN)_6$	13746-66-2	4	acetone (85)
			$AgNO_3$	7761-88-8	2	acetone (88)
			$CuSO_4$	7758-98-7	2	acetone (89)
2	benzyl alcohol	100-51-6	$K_3Fe(CN)_6$		4	benzalehyde (86)
			$AgNO_3$		1	benzaldehyde (82)
			$CuSO_4$		2	benzaldehyde (80)
			$K_3Fe(CN)_6$[e]		5	benzyl alcohol (89)
3	benzhydrol	91-01-0	$K_3Fe(CN)_6$		4	benzophenone (78)
			$AgNO_3$		2	benzophenone (84)
4	phenylmethylcarbinol	98-85-1	$K_3Fe(CN)_6$		5	acetophenone (92)
			$AgNO_3$		2	acetophenone (96)
5	cylcopentanol	96-41-3	$K_3Fe(CN)_6$		3	cyclopentanone (90)
			$AgNO_3$		1.5	cyclopentanone (87)
6	cyclohexanol	108-93-0	$K_3Fe(CN)_6$		4.5	cyclohexanone (85)
			$AgNO_3$		1.5	cyclohexanone (90)
			$CuSO_4$		2	cyclohexanone (95)
			$AgNO_3$[e]		4	cyclohexanol (93)
7	cycloheptanol	502-41-0	$K_3Fe(CN)_6$		5	cycloheptanone (85)
			$AgNO_3$		2	cycloheptanone (87)
8	norborneol	1632-68-4	$K_3Fe(CN)_6$		6	camphor (86)
9	borneol	507-70-0	$AgNO_3$		2.5	camphor (88)
10	menthol	1490-04-6	$K_3Fe(CN)_6$		4	methone (90)
			$AgNO_3$		1	methone (95)
11	benzoin	119-53-9	$K_3Fe(CN)_6$		5	benzil (92)
			$AgNO_3$		2	benzil (96)
12	1,4-butanediol[d]	110-63-4	$AgNO_3$		1	butane-1,4-dial (91)

[a] The solvent is a mixture of Me_2SO and water in a 2:1 (v/v) ratio, unless otherwise specified. [b] The ratio of concentrations between alcohol and oxidant is 1:1.5 unless otherwise stated. [c] The number in parentheses indicates the percentage of the product; the product is identified as the corresponding 2,4-DNP derivative and characterized by its melting point with the reported ones; the yields are also based on the amount of 2,4-DNP derivative formed. [d] The solvent is water only. [e] The reactions were carried out in the presence of oxygen.

our results will be communicated once a reasonable conclusion can be arrived at.

From the standpoint of organic chemistry, the information and the knowledge that primary alcohols are oxidized only to the aldehyde and not to the acids in quantitative yields are useful. Run numbers 2 and 12 prove this. It is also evident from our studies that the excited Cu^{2+} and Ag^+ ions are stronger oxidizing agents than the excited Fe^{3+} ion as indicated by the irradiation time. Further research on the oxidation of diols with two electron oxidants are under investigation.

Experimental Section

A. General Procedure for Photostimulated Oxidation Reaction. A water/Me_2SO mixture in the ratio of 1:2 (v/v) is used to dissolve both the oxidants and alcohols. The reactions are carried out in a quartz vessel using 350-nm lamps in a Rayonet photochemical reactor under nitrogen atmosphere. The completion of the reactions was checked by the formation of both the oxidized product from the alcohols and the reduced ions from the metal ions. The quantitative estimations of the products were done with 2,4-DNP by the precipitation of the derivative of the corresponding ketones. The melting points of these compounds were checked with the reported ones and the products were thus characterized. The presence of the reduced oxidants was checked qualitatively. The ratio of concentrations between alcohol and oxidant is 1:1.5 and for the diol the ratio is 1:3.

B. Oxidation of Benzhydrol by $FeCl_3$ in Aqueous Me_2SO. In a typical reaction, 0.15 g (0.000 815 3 mol) of benzhydrol was dissolved in 10 mL of Me_2SO. Anhydrous $FeCl_3$ (0.1982 g = 0.001 223 mol) was dissolved in 5 mL of water. The aqueous $FeCl_3$ solution was added to the alcohol dissolved in Me_2SO. To the homogeneous solution, pure nitrogen, was passed for 10 min. The reaction mixture, taken in a quartz vessel, was irradiated with a 350-nm lamp for about 3 h.

After irradiation, the product was identified as the corresponding 2,4-DNP derivative. The formation of a deep blue color by the addition of $K_3Fe(CN)_6$ showed the presence of Fe^{2+}.

C. Oxidation of Isopropyl alcohol by $K_3Fe(CN)_6$ in Pure Water. Isopropyl alcohol (0.008 333 mol) was dissolved in 20 mL of water. Exactly 3.137 g of $K_3Fe(CN)_6$ (0.0125 mol) was added to the above solution. Nitrogen gas, free from moisture, air, and other ingradients, was passed through the solution for about 13 min. The reaction mixture was irradiated with the 350-nm lamp in a Rayonet photochemical reactor for about 4 h under N_2.

After irradiation a brown colored precipitate was thrown out of the reaction mixture and that was filtered and tested for the presence of ferrous ion using $FeCl_3$. The product was characterized by the melting point of the 2,4-DNP derivative in comparison with the reported one for acetone.

D. Oxidation of Cyclohexanol by $AgNO_3$ in Aqueous Me_2SO. Silver nitrate, 1.275 g (0.007 501 mol), was dissolved in 5 mL of conductivity water. Cyclohexanol (0.5 g; 0.005 mol) was dissolved in 15 mL of Me_2SO. The aqueous silver nitrate solution was added to the alcohol in Me_2SO. Nitrogen gas free from oxygen and moisture was bubbled through the solution for 15 min. The irradiation was carried out using the 350-nm lamp for 1.5 h under N_2. The oxidized product was characterized as the corresponding 2,4-DNP derivative. Silver was precipitated after irradiation.

E. Oxidation of Phenylmethylcarbinol by $CuSO_4$. In a typical reaction, 1.5350 g (0.006 148 mol) of $CuSO_4 \cdot 5H_2O$ was dissolved in 10 mL water. Exactly 0.5 g of (0.004 099 mol) α-phenylmethylcarbinol was dissolved in 20 mL of Me_2SO. The aqueous copper sulfate was added to the alcohol in Me_2SO. The resultant homogeneous solution was irradiated under nitrogen atmosphere in a Rayonet photochemical reactor using 350-nm lamps for 3 h.

After irradiation, a white insoluble precipitate was thrown out. It answered the test for Cu^+. The chemical nature of the precipitate was not known. The product was identified as the corresponding 2,4-DNP derivative and characterized by the melting point with the reported one for acetophenone.

F. Oxidation of 1,4-Butanediol with Silver Nitrate. 1,4-Butanediol, 0.5 g (0.005 556 mol), was dissolved in 30 mL of (conductivity) water. Silver nitrate (1.417 g, 0.008 mol) was added. Pure nitrogen gas was bubbled through the reaction mixture for about 13 min. The irradiation was carried out at 350 nm in a Rayonet photochemical reactor for about 1 h under N_2. The formation of the black precipitate (Ag^0) indicated the completion of the reaction. The product 1,4-

butanedial was identified as the corresponding 2,4-DNP derivative.

G. Preparation of 2,4-DNP Reagent. Powdered 2,4-DNP (10 g) was suspended in 30 mL of methanol under stirring. To this was added cautiously 20 mL of concentrated H_2SO_4. The solution was filtered while it was warm and the filtrate was cooled.

Reactions under oxygen and air were done similarly.

Acknowledgment. We thank Professor N. Venkatasubramanian, Vivekananda College, Madras for helpful guidance. We also thank Dr. M. Srinivasan, IIT, Madras for letting us use the photochemical reactor. S.R. thanks CSIR for pool-officership.

References and Notes

(1) The first paper in the series is in press, *Ind. J. Chem.*
(2) Part of the master of science project work, submitted to the University of Madras in May, 1978.
(3) V. I. Stenberg, S. P. Singh, N. K. Narain, and S. S. Parmar, *J. Org. Chem.*, **42**, 171 (1977).
(4) (a) A. I. Kryukov, L. V. Nazario, and B. Y. Dais, *Ulkr. Khim. Zh.* (*Russ. Ed.*), **29**, 812 (1963); (b) V. Bulzari and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970, pp 178–83; (c) T. S. Gliknas, B. Y. Dais, and B. F. Kutsaya, *Zh. Fiz. Khim.*, **22**, 906 (1948).
(5) G. J. Brealey, M. G. Evans, and N. Uri, *Nature* (*London*), **166**, 959 (1950).
(6) G. J. Brealey and N. Uri, *J. Chem. Phys.*, **20**, 257 (1952).

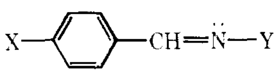
Electronic Substituent Effects on Nitrogen-15 Shieldings of *N*-(Arylmethylidene)cyclohexanamine Hydrotrifluoroacetates[1a]

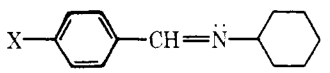
Robert E. Botto[1b] and John D. Roberts*

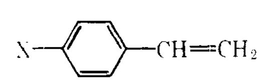
Contribution No. 5846 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

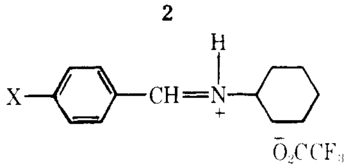
Received August 1, 1978

An earlier ^{15}N NMR study[2] of several series of para-substituted *N*-(arylmethylidene)amines 1 and 2 has shown that


1


2


3


4

the nitrogen shifts are sensitive to the electronic influence of the ring substituents (X), as reflected by the Hammett σ substituent parameters. Reasonable linear correlations could also be obtained for the nitrogen shifts of compounds in each series and the β-carbon shieldings of 4-substituted ethenylbenzenes 3, with the changes in the ^{15}N shifts generally being about twice that of the ^{13}C shifts with respect to the substituent effects. To determine whether the greater sensitivity of the nitrogen shifts arises predominantly from a substituent-induced perturbation of the nitrogen unshared pair of electrons, we have measured ^{15}N chemical shifts of a series of para-substituted *N*-(arylmethylidene)cyclohexanamine hydrotrifluoroacetates 4.

The natural abundance ^{15}N spectra were recorded on a Bruker WH-180 spectrometer operating at 18.25 MHz. The optimum conditions for observing imino nitrogens in *N*-(arylmethylidene)cyclohexanamines were a 70° pulse angle, a repetition rate of 30 s, and gated proton decoupling (no NOE). The conditions employed to obtain spectra of their corresponding hydrotrifluoroacetates were a 27° pulse angle, a repetition rate of 2 s, and continuous broad-band proton irradiation. The chemical shifts and one-bond ^{15}N–H coupling constants are summarized in Table I.

Table I. Nitrogen-15 Chemical Shifts of *N*-(Arylmethylidene)cyclohexanamines 2 and Their Hydrotrifluoroacetates 4 [a]

X	4 registry no.	chemical shift chloroform[b]	chemical shift trifluoroacetic acid ($^1J_{^{15}N-H}$, Hz)
OCH_3	68051-12-7	38.5	187.7 (91.1)
CH_3	68051-13-8	33.9	181.4 (92.0)
H	68051-14-9	30.2	177.4 (90.3)
Cl	68051-15-9	28.1	175.7 (88.5)
NO_2[c]	68051-16-1	14.7	164.1 (92.0)

[a] All chemical shifts are given in ppm upfield from an external 1.0 M $D^{15}NO_3$ capillary. Measured as 20 mol % solutions in chloroform and trifluoroacetic acid. [b] Data from ref 2. [c] δ $^{15}N(NO_2)$ = 6.8 ppm in chloroform; no signal observed in trifluoroacetic acid.

The ^{15}N shifts of *N*-(arylmethylidene)cyclohexanamines 2 in chloroform cover the range 14.7 to 38.5 ppm. When these compounds are dissolved in trifluoroacetic acid, there is a very large diamagnetic shift (~150 ppm) of the nitrogen resonances as expected for protonation of the nitrogen unshared electron pair, with the ^{15}N shift range becoming 164.1 to 187.7 ppm. Formation of the hydrotrifluoroacetate salts 4 is assured by observation of one-bond ^{15}N–H coupling constants which are of the magnitude expected for hydrogen attached to nitrogens which are sp^2 hybridized.[3] No trends are evident for these couplings with Hammett substituent parameters. No two-bond ^{15}N–C–H couplings were observed, and this is in accord with a previous investigation of structurally similar compounds which suggests that these two-bond couplings should probably be small (<1 Hz).[4]

The large upfield protonation shifts for the change 2 to 4 are best accounted for by changes in the paramagnetic screening contribution (σ_A^{para}), which appears to dominate the total screening of nitrogen nuclei.[5] The paramagnetic expression depends, in part, on contributions from the average electronic excitation energy, ΔE_{av}.[6] Thus, for the specific case of a nitrogen atom in a C–N double bond as in 1, mixing into the ground-state wave function in an external field of an electronic configuration corresponding to a low lying n → π^* transition is expected to lead to a paramagnetic circulation of electrons around the nitrogen and thereby decrease the shielding of the nitrogen nucleus. Because there is no unshared electron pair in the protonated imines, the ΔE_{av} term corresponding to this effect will be much less important. The extent of this paramagnetic contribution to the shielding of nitrogen nuclei in compounds containing C–N double bonds can be seen by comparing changes in ^{15}N and ^{13}C shieldings for the structural change $C_6H_5CH_2Y^*(H)_nR \rightarrow C_6H_5CH{=}Y^*(H)_{n-1}R$, where * denotes the nucleus undergoing the NMR transition. The shift to lower field (~250 ppm) for Y = ^{15}N for this change is about twice that for Y = ^{13}C.[7] However, when the imines are protonated and become isoelectronic with the corresponding phenylethenes, the downfield shifts of ^{15}N and ^{13}C nuclei associated with this change are then quite similar.

As we have said, the ^{15}N shieldings of *N*-(arylmethylidene)cyclohexanamines 2 correlate quite well with Hammett σ parameters, yet the ^{15}N shifts appear to be twice as sensitive