or antibonding properties of the highest occupied MO are not a helpful guide to the over-all energy change, and, in general, one cannot depend on the HOCMO predicting the over-all bond order or energy change on bonding.[11] A safer approach is the consideration of bond order[9,12] and energy change.[4,5]

Acknowledgment. Support of this research by the National Science Foundation, NIH Grant GM07487, and the Wisconsin Alumni Research Foundation is gratefully acknowledged.

(11) (a) In the case of 1,5 bonding of hexatriene the total bond order prior to molecular change is zero and is of no help. Subsequent to slight molecular change the bond order is helpful. (b) It can be shown that for a system of p orbitals arranged so that alternating atoms are starred except for two adjacent starred positions, the Möbius and Hückel versions will have energy levels which are mirror images of one another, and coefficients are simply related.

(12) H. E. Zimmerman, Abstracts, 17th National Organic Chemistry Symposium, Bloomington, Indiana, June 1961, p 31.

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The Reactivity of Electrons Produced in the γ-Radiolysis of Aliphatic Alcohols[1]

Sir:

The reactions of solvated electrons with aromatic hydrocarbons in aqueous solution conform to the general pattern of bimolecular nucleophilic substitution, SN2.[2] The solvated electron is an important intermediate in the radiolysis of alcoholic solutions,[3–9] and it would be of interest to determine whether this species fits a pattern similar to that of the hydrated electron, and if so, the influence of the change in solvent on reactivity.

It has been demonstrated[9] that nitrous oxide is a specific scavenger for solvated electrons produced in the radiolysis of 2-propanol solutions, and a convenient method for determining the reactivity of solute substrates has been suggested.[9] This method involves the measurement of the yield of molecular nitrogen, $G(N_2)$, in competitive experiments in which a solution of nitrous oxide and the substrate is irradiated. The difference between $G(N_2)$ and the nitrogen yield in the radiolysis of a solution containing the same concentration of nitrous oxide alone, $G(N_2)_0$, gives a measure of the electrons scavenged by the substrate, and hence its reactivity relative to nitrous oxide. Such competitive experiments have now been carried out with a number of monosubstituted benzenes in 2-propanol and methanol,[10] and the results are listed in Table I.

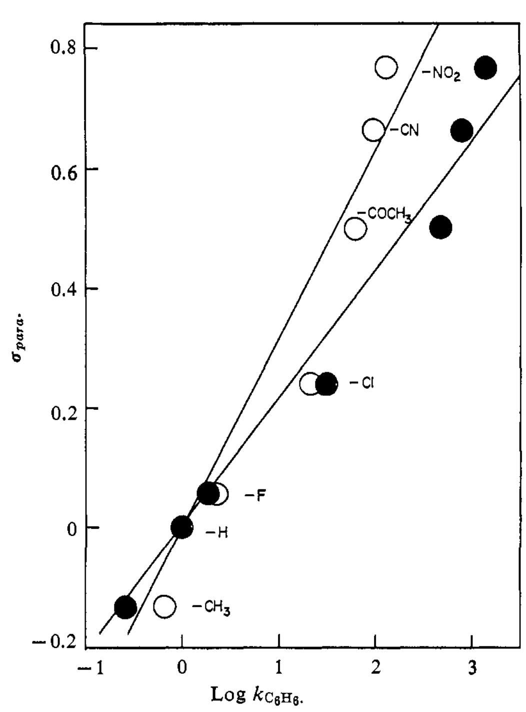

Figure 1. Plot of Hammett σ_{para} functions[11] *vs.* log $k_{C_6H_6}$ values obtained in 2-propanol and methanol. ○, 2-propanol; ●, methanol.

In Figure 1 the logarithm of the rate constants of the monosubstituted benzenes normalized to that of benzene, log $k_{C_6H_6}$, are plotted against the respective Hammett σ_{para} functions.[11] A satisfactory linear correlation is obtained in both solvents. This result is in accord with the rate-determining step in the reaction of the solvated electron with aromatic compounds being the localized attack on the aromatic nucleus.[2] The ρ value for the reaction in 2-propanol and methanol is 3.1 and 4.7, respectively.

Table I. Reactivity Relative to Nitrous Oxide of Monosubstituted Benzenes in 2-Propanol and Methanol

Aromatic substrate	$k_{N_2O}{}^a$	
	2-Propanol	Methanol
Toluene	1.4×10^{-2}	7.2×10^{-4}
Benzene	2.1×10^{-2}	2.9×10^{-3}
Fluorobenzene	5.0×10^{-2}	5.9×10^{-3}
Chlorobenzene	5.4×10^{-1}	9.5×10^{-2}
Acetophenone	1.7	1.8
Benzonitrile	1.9	2.1
Nitrobenzene	2.3	4.1

^{a} Reactivity relative to nitrous oxide.

The energy of an electron in a dipolar medium involves the term $(1/D_{op} - 1/D_s)$,[12] where D_{op} and D_s are the optical and static dielectric constants, respectively. D_{op} generally has values near unity, so that as D_s increases the energy of the solvated electron decreases. The static dielectric constant at room temperature of 2-propanol and methanol are 19 and 33, respectively,[13] and the hypsochromic shift observed

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(1) This work was performed during the tenure of an Israel Atomic Energy Commission Fellowship.

(2) M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).

(3) J. H. Baxendale and F. W. Mellows, *ibid.*, **83**, 4720 (1961).

(4) G. E. Adams and R. D. Sedgwick, *Trans. Faraday Soc.*, **60**, 865 (1964).

(5) J. J. J. Myron and G. R. Freeman, *Can. J. Chem.*, 43, 381 (1965).

(6) E. Hayon and M. Moreau, *J. Phys. Chem.*, **69**, 4053 (1965).

(7) I. A. Taub, D. A. Harter, M. C. Sauer, and L. M. Dorfman, *J. Chem. Phys.*, 41, 979 (1965).

(8) H. Seki and M. Imamura, *Bull. Chem. Soc. Japan*, **38**, 1229 (1965).

(9) W. V. Sherman, *J. Phys. Chem.*, **70**, 667 (1966).

(10) Full details of the radiolysis of the nitrous oxide–methanol system will be published elsewhere.

(11) The σ values are those given in the review by H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

(12) J. Jortner, *Radiation Res. Suppl.*, 4, 24 (1964), and references quoted therein.

(13) F. Buckley and A. A. Maryott, National Bureau of Standards Circular 583, U. S. Government Printing Office, Washington, D. C., 1958.

for the optical absorption maxima of the electron in these solvents[14] reflects the increasing stabilization of the electron by solvation. It is significant that the sequence of increasing dielectric constants is paralleled by increasing ρ values for the reaction. The greater sensitivity to substituent effects observed in solvents of larger static dielectric constant reflects an increasing energy of activation, and hence it is reasonable to conclude that the transition state for the substitution reaction in alcohols

$$e^-_{\text{solv}} + C_6H_5X \longrightarrow C_6H_5X^-$$

is less stabilized by solvation than the electron.

The similarity between the ρ value in methanol and that found for the electron in water, 4.8,[2] is noteworthy and in accord with the previously noted[7] agreement between the rate constants, determined by the pulse radiolysis technique, of benzyl chloride and oxygen in these two media. Hence the apparent correlation between the ρ value and dielectric constant observed in the two alcohols does not extend to reactions in water. Correspondingly, the correlation between the optical transition energy of the solvated electron and dielectric constant observed in five aliphatic alcohols (including methanol and 2-propanol)[14] was also found to break down when extended to the hydrated electron.

(14) M. C. Sauer, S. Arai, and L. M. Dorfman, *J. Chem. Phys.*, 42, 708 (1965).

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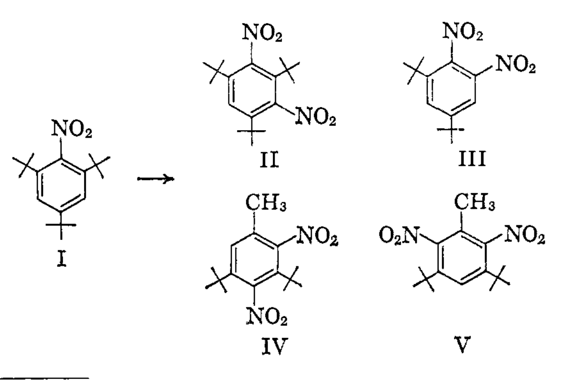
Reactions of Cyclohexadienyl Cations. Molecular Rearrangement Attendent Aromatic Nitration[1]

Sir:

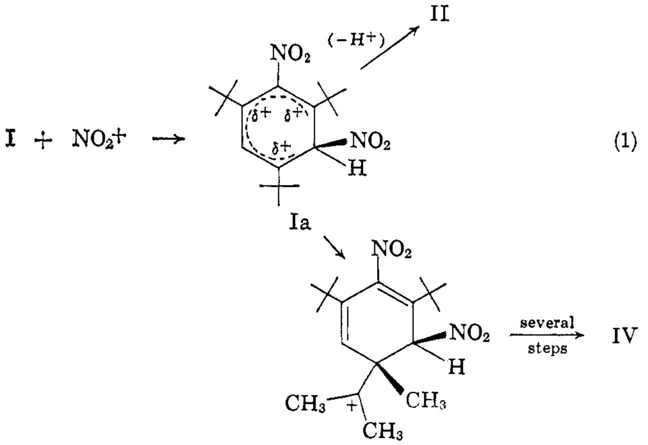
The products of nitration of 2,4,6-tri-*t*-butylnitrobenzene (I) dictate an unusual molecular rearrangement with important mechanistic implications. Reaction of I with 90% nitric acid at 0° affords four major products: 1,3-dinitro-2,4,6-tri-*t*-butylbenzene (II), 59%; 1,2-dinitro-3,5-di-*t*-butylbenzene (III), 5%; 2,4-dinitro-3,5-di-*t*-butyltoluene (IV), 34%; and 2,6-dinitro-3,5-di-*t*-butyltoluene (V), 2%. The same products but with different distribution are obtained by nitration of I with other nitrating agents, such as nitronium tetrafluoroborate.



The products III, IV, and V were isolated from the ethanol-soluble fraction of the crude nitration product and separated by a combination of column chromatography over alumina and preparative gas–liquid chromatography. Initial characterization of these compounds was effected by means of their definitive nmr spectra[2] and subsequently confirmed by mass spectral and elemental analyses. Syntheses of compounds identical in all respects with IV and V by stepwise nitration of 3,5-di-*t*-butyltoluene completed the proof of structure.[3]

III is almost certainly formed by direct nitrodealkylation. It is surprising perhaps that the amount of nitrodealkylation is so small.[4]

The transformation of I to IV and V appears to be without direct precedent. In the absence of any evidence of prior acid-catalyzed rearrangement of I, it is necessary to assume that IV and V are formed during nitration. A possible mechanism for the replacement of a *t*-butyl group by methyl which meets this condition is one involving a rearrangement of the intermediate alkylcyclohexadienyl cation (Ia) followed by oxidative cleavage of the isopropyl moiety (eq 1).



(1)

The intermediate role of cyclohexadienyl cations (σ complexes) in aromatic electrophilic substitution processes is well established. Energetically favorable

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] The predominantly singlet spectra at 60 Mc in CCl_4 referenced to TMS (δ values) are as follows together with relative area and assignment: for I, 1.32 (9 H), *p-t*-Bu; 1.38 (18 H), *o-t*-Bu; 7.42 (2 H), ArH; for II, 1.39 (18 H), 4,6-*t*-Bu; 1.45 (9 H), 2-*t*-Bu; 7.72 (1 H), ArH; for III, 1.40 (9 H), 5-*t*-Bu; 1.43 (9 H), 3-*t*-Bu; 7.87 (2 H), AB quartet, $J = 2$ cps, ArH; for IV, 1.37 (9 H), 5-*t*-Bu; 1.43 (9 H), 3-*t*-Bu; 2.23 (3 H), doublet, $J = 0.6$ cps, 1-Me; 7.47 (1-H), quartet, $J \simeq 0.6$ cps, ArH; for V 1.39 (18 H), 3,5-*t*-Bu; 2.05 (3 H), doublet, $J \simeq 0.5$ cps, 1-Me; 7.57 (1-H), quartet, $J \simeq 0.5$ cps, ArH.

[3] J. Geuze, C. Ruinard, J. Soeterbroek, P. E. Verkade, and B. M. Wepster *Rec. Trav. Chim.*, 75, 305 (1956).

[4] Nitrodealkylation does not appear to be an important process in the nitration of either 1,3,5-triisopropylbenzene or 1,3,5-tri-*t*-butylbenzene. Although a report by Olah and Kuhn would indicate that both of these hydrocarbons undergo nitrodealkylation upon nitration with nitronium tetrafluoroborate in sulfolane, reinvestigation of these reactions shows that the normal nitration products are formed with no detectable (<1%) nitrodealkylation product.[5] These results are quite similar to those obtained using more conventional nitration procedures.[6] However, nitrodealkylation is an important process in the nitration of 2,4,6-tri-*t*-butylbromobenzene and 2,4,6-tri-*t*-butylfluorobenzene where 2-nitro-4,6-di-*t*-butylbromobenzene and 4-nitro-2,6-di-*t*-butylfluorobenzene are found to be the principal nitration products.

[5] (a) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, 86, 1067 (1964). (b) Professor Olah, in a private communication, has indicated that the results of this reinvestigation are correct and that the error in the initial study was due to the nature of the analytical method.

[6] (a) A. Newton, *J. Am. Chem. Soc.*, 65, 2434 (1943); (b) P. D. Bartlett, M. Roha, and R. M. Stiles, *ibid.*, 76, 2349 (1954); (c) B. M. Wepster, *et al.*, *Rec. Trav. Chim.*, 77, 491 (1958); (d) P. C. Myhre, *Acta Chem. Scand.*, 14, 219 (1960).