istered by the American Chemical Society, and the Robert A. Welch Foundation for financial support.

* Address correspondence to this author.

J. Wristers, Lazaro Brener, R. Pettit*
Department of Chemistry, University of Texas
Austin, Texas 78712
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Electrophilic Aromatic Substitution Reactions.
An Ion Cyclotron Resonance Study

Sir:

We have observed that ions to which electrophilic behavior in solution is ascribed form ionic complexes with benzene at relatively low pressures (ca. 4×10^{-5} Torr) at 30 eV in patterns reminiscent of the first step of textbook mechanisms for electrophilic substitution (eq 1).[1] The first step of this process can be

$$E^+ + C_6H_6 \longrightarrow C_6H_6E^+ \longrightarrow C_6H_5E + H^+ \qquad (1)$$
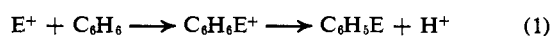
approximated in an ion–molecule reaction involving attack of a nucleophile on benzene, frequently in the form of the transfer of the electrophile from a Lewis base to benzene, a process conveniently studied by ion cyclotron resonance (icr) spectrometry.[2]

We find through the icr technique that benzene (10^{-5} Torr) can be nitrated by a variety of reagents ($2–4 \times 10^{-5}$ Torr). As possible reagents for the nitration of benzene at these pressures, we have examined NO_2 itself as well as selected ions formed in the icr chemistry of alkyl nitrates (eq 2 and 3).[3] The

$$C_2H_5ONO_2 \cdot^+ \longrightarrow CH_2 = \overset{+}{O}NO_2 \longleftarrow CH_3ONO_2 \cdot^+ \qquad (2$$

$$C_2H_5\overset{+}{O}NO_2 \longrightarrow H\overset{+}{O}NO_2 \qquad (3)$$
$$\quad H \qquad\qquad H$$

origin of the m/e 130 ion ($C_6D_6NO_2^+$) formed in a mixture of C_6D_6 and NO_2 is found through ion cyclotron double resonance (icdr) not to correspond to the product of electrophilic substitution, for its primary precursor is the linear[4] $C_6D_6 \cdot^+$ not NO_2^+ (eq 4).[5] However, icdr studies on mixtures of C_6D_6 with CH_3ONO_2 or $C_2H_5ONO_2$ show that here the m/e 130 ion is formed not from

$$C_6D_6 \cdot^+ + NO_2 \longrightarrow C_6D_6NO_2^+ \qquad (4)$$

$C_6D_6 \cdot^+$ but, to a substantial degree, from $H_2NO_3^+$ (m/e 64), $CH_2ONO_2^+$ (m/e 76), or $CH_3CHONO_2^+$ (m/e 90). The protonated esters are also able to nitrate benzene. These processes correspond to the first step of eq 1, electrophilic addition.

A further ion–molecule product of these systems is $C_6D_6O \cdot^+$ (m/e 100), whose origin is principally the m/e 46 ion, NO_2^+. If the structure of $C_6D_6O \cdot^+$ is that of phenol, this electrophilic substitution (eq 5) may be

(1) For a recent review, see E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964).

(2) For a description of the technique see (a) J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968); (b) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *ibid.*, **89**, 4569 (1967).

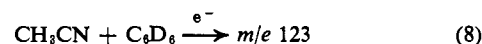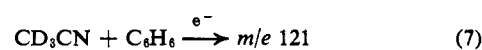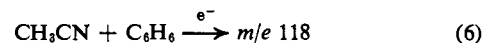(3) P. Kriemler and S. E. Buttrill, Jr., *ibid.*, **92**, 1123 (1970).

(4) *Cf.* J. Momigny, L. Brakier, and L. D'Or, *Bull. Cl. Sci. Acad. Roy. Belg.*, **48**, 1002 (1962).

(5) This m/e 130 peak is weak (<1% of the intensity of the m/e 84 peak) under conditions where the m/e 130 peak in the C_6D_6–CH_3ONO_2 and C_6D_6–$C_2H_5ONO_2$ systems is much larger; it must be collision stabilized, and the process is not important under these conditions.

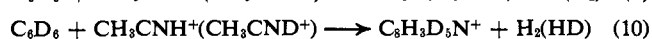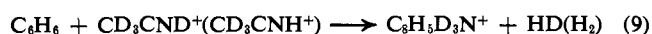$$C_6D_6 + NO_2^+ \longrightarrow C_6D_6O \cdot^+ + NO \qquad (5)$$

analogous to the probable first step in the formation of nitrophenols upon irradiation of mixtures of benzene and NO_2.[6,7] No information on its structure, as with most ions, is readily available, however.

In a search for other possible electrophilic substitution, mixtures of deuterated and undeuterated acetonitrile and benzene (eq 6–8) under conditions

$$CH_3CN + C_6H_6 \xrightarrow{e^-} m/e\ 118 \qquad (6)$$

$$CD_3CN + C_6H_6 \xrightarrow{e^-} m/e\ 121 \qquad (7)$$
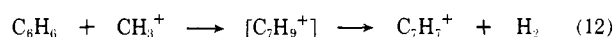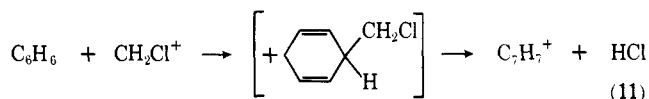
$$CH_3CN + C_6D_6 \xrightarrow{e^-} m/e\ 123 \qquad (8)$$

similar to those above produce an ion which corresponds (in mass) to that expected ($C_6H_6CH_2CN^+$) from cyanomethylation. However, icdr shows that this electrophilic addition is not a simple attack of cyanomethyl cation, CH_2CN^+, on benzene, for the attacking species is protonated acetonitrile, CH_3CNH^+.[8,9] The reaction therefore could correspond to a Hoesch synthesis[10] at its first step involving benzene, and the gaseous ionic products correspond to loss of a hydrogen atom from benzene and the NH hydrogen from CH_3CNH^+ in the collision complex (eq 9 and 10),

$$C_6H_6 + CD_3CND^+(CD_3CNH^+) \longrightarrow C_8H_5D_3N^+ + HD(H_2) \quad (9)$$
$$C_6D_6 + CH_3CNH^+(CH_3CND^+) \longrightarrow C_8H_3D_5N^+ + H_2(HD) \quad (10)$$

perhaps in a four-center process to yield $C_6H_5 \cdot C = N \cdot^+CH_3$.

A third electrophilic reaction system, methyl chloride and benzene, also includes reactions corresponding to the addition step of electrophilic aromatic substitution; in each case the required expulsion of a neutral molecule masks the electrophilic attack, for no simple addition product is observed at our pressures. One pathway is analogous to the Blanc chloromethylation reaction,[11] for the final product is formed from attack of CH_2Cl^+ on benzene (eq 11). Another pathway corresponds to the Friedel–Crafts reaction[12] at first, but again the gaseous ionic and solution routes separate after the initial attack of the electrophile on benzene (eq 12). Equation 11 is exothermic by 59 or

$$C_6H_6 + CH_2Cl^+ \longrightarrow \left[+ \underset{H}{\overset{CH_2Cl}{\bigcirc\!\!\!\!<}} \right] \longrightarrow C_7H_7^+ + HCl \qquad (11)$$

$$C_6H_6 + CH_3^+ \longrightarrow [C_7H_9^+] \longrightarrow C_7H_7^+ + H_2 \qquad (12)$$

52 kcal/mol if $C_7H_7^+$ is benzyl or tropylium;[13] eq 12

(6) W. Kemula and A. Grabowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **8**, 517 (1960).

(7) Note also the thermolysis of nitrobenzene: E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 273 (1969).

(8) CH_3CNH^+ is found in the ion–molecule chemistry of acetonitrile: G. A. Gray, *J. Amer. Chem. Soc.*, **90**, 2177 (1968).

(9) Icdr also indicates that $C_6H_6CH_2CN^+$ is also produced by an additional pathway, attack of $C_6H_5^+$.

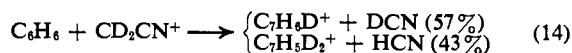(10) K. Hoesch, *Chem. Ber.*, **48**, 1122 (1915).

(11) G. Blanc, *Bull. Soc. Chim. Fr.*, **33**, 313 (1923).

(12) C. Friedel and J. M. Crafts, *Compt. Rend.*, **84**, 1292, 1450 (1877).

(13) In unimolecular decompositions, $C_7H_7^+$ which decomposes is tropylium.[14] In high-pressure chemical ionization studies of toluene,[15] formation by $C_7H_7^+$ by hydrogen abstraction does not involve randomization before abstraction. We see no further fragmentation of $C_7H_7^+$.

(14) (a) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York,

is exothermic by 71 or 64 kcal/mol.[16] The $C_7H_7^+$ species is also formed in the acetonitrile–benzene system (eq 13–15) by the electrophilic attack of CH_2CN^+

$$C_6H_6 + CH_2CN^+ \longrightarrow C_7H_7^+ + HCN \qquad (13)$$

$$C_6H_6 + CD_2CN^+ \longrightarrow \begin{cases} C_7H_4D^+ + DCN \ (57\%) \\ C_7H_5D_2^+ + HCN \ (43\%) \end{cases} \qquad (14)$$

$$C_6D_6 + CH_2CN^+ \longrightarrow \begin{cases} C_7HD_6^+ + HCN \ (52\%) \\ C_7H_2D_5^+ + DCN \ (48\%) \end{cases} \qquad (15)$$

on benzene; again, this represents the product of a loss of a small neutral from the intermediate addition product. Scrambling data indicate that more hydrogen is lost from the activated complex than from the acetonitrile-derived species than would be expected on the basis of complete randomization of all eight hydrogens.

Ion cyclotron resonance is of great value in demonstrating that some ion–molecule products in these mixtures are indeed products of initial electrophilic aromatic addition, apparently similar to the first step in solution electrophilic aromatic substitution, after which gaseous and solution pathways diverge. Further studies of electrophilic aromatic substitution reactions, substituent effects on them, and the structure of $C_7H_7^+$ formed by ion–molecule reactions will be discussed in full papers.

N. Y., 1963, p 453; (b) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

(15) F. H. Field, *ibid.*, **89**, 5328 (1967).

(16) Data taken from (a) "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969; (b) Handbook of Chemistry and Physics, 49th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968.

(17) Research Fellow of the Alfred P. Sloan Foundation, 1969–1971.
* Address correspondence to this author.

Steven A. Benezra, Michael K. Hoffman
Maurice M. Bursey*,[17]

Venable Chemical Laboratory, The University of North Carolina
Chapel Hill, North Carolina 27514
Received August 25, 1970

# Flash Photolysis of a Conjugated Cyclohexenone. A Reinvestigation[1]

Sir:

The results of a flash photolytic investigation of the conjugated cyclohexenone I were recently reported by Rämme, Strong, and Richtol (RSR).[2] These results were most unusual and surprising, especially in relation to the steady-state photolytic studies previously reported on I by Zimmerman and Chapman and their

(1) Part XXVIII of a series on the photochemistry of unsaturated ketones in solution. Part XXVII: D. I. Schuster and W. C. Barringer, *J. Amer. Chem. Soc.*, in press.

(2) G. Rämme, R. L. Strong, and H. H. Richtol, *ibid.*, **91**, 5711 (1969).

coworkers[3,4] and studies of other cyclohexenones reported by Bellus, Kearns, and Schaffner[5] and by Schuster and Brizzolara.[6]
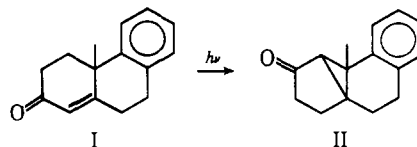
It had been found earlier that the inefficient photoisomerization I → II as well as photopinacolization of I in 2-propanol proceed from a triplet state (or two triplet states in thermal equilibrium) which can be quenched by naphthalene.[3] The lifetime of the triplet in benzene from the quenching data was estimated as $\sim 10^{-8}$ sec.[3] Phosphorescence at low temperature showed a 0–0 band at 401 nm (71 kcal/mol).[3] This value is in agreement with the phosphorescence observed more recently with a number of other fused-ring cyclohexenones,[7] which has been convincingly attributed[7] to emission from the lowest π,π triplet, which in these systems is below the lowest n,π triplet state.

On the basis of the above, it was surprising that on flashing I in a variety of solvents, including good as well as poor hydrogen donors, two transients were observed.[2] A short-lived transient was observed (τ 100–400 μsec), λ_{max} 430 nm, which exhibited first-order decay, and which could be quenched by oxygen but *not by naphthalene*. In fact, the lifetime of the naphthalene triplet was decreased as the concentration of I was increased, indicating triplet energy transfer from, rather than to, naphthalene. The second transient, which showed a long lifetime on the order of many milliseconds, was a minor component in the visible region, and increased in intensity at lower wavelengths. Finally, the emission data previously reported[3] could not be duplicated, and the weak emission observed by RSR[2] was tentatively ascribed to an impurity. In order to explain these observations, RSR[2] postulated that the reactions of I proceeded exclusively *via* an upper triplet state, and that there was a lower triplet (the short-lived transient) which was unreactive, energetically situated below the lowest naphthalene triplet. The long-lived transient was assumed to be the protonated ketyl radical formed by hydrogen abstraction, although the formation of this species (albeit in decreased amounts) in poor hydrogen donor solvents passed without comment.

Since all other cyclohexenones studied thus far[3–6] have very close-lying n,π and π,π triplets, with the lowest triplet located approximately 70 kcal/mol above the ground state,[3,5] it seemed most strange that I should have such different characteristics. It seemed to us that the most reasonable explanation for the observations of RSR[2] was that the observed transients

(3) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 159, 1965 (1966).

(4) O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *ibid.*, **88**, 161 (1966).

(5) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

(6) D. I. Schuster and D. F. Brizzolara, *J. Amer. Chem. Soc.*, **92**, 4357 (1970).

(7) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968); G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).