constant for 17α-methyltestosterone is 0.57, *i.e.*, $K_{AMT} = 0.57$. The carbonyl groups of both compounds have association constants of 0.47, *i.e.*, $K_{BT} = K_{BMT} = 0.47$.

The graphical reduction of the data presented in this report is susceptible to computerization, but such efforts should probably be approached with caution. Difficulties include the amplified effect of uncertainties for small distances (3–4 Å) and problems associated with the estimation of contact-shift contributions to protons near coordination sites. Angle functions assumed constant in this study may be important in other systems.[10,11] Operations that can be performed visually in a graphical reduction of data require careful programming in a computer analysis.

Acknowledgments. Discussions with Dr. R. E. Beyler were extremely helpful. The Varian HA-100 nmr spectrometer was purchased with the aid of a grant from the National Science Foundation.

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[10] George H. Wahl, private communication. Angle factors appear to be important in shifts induced in the pmr spectrum of 2-adamantanol.

[11] Demarco, Elzey, Lewis, and Wenkert have studied europium-induced shifts in alcohols[12] and steroids.[13] Their findings also indicate some angular dependence in observed shifts.

[12] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

[13] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, **92**, 5737 (1970).

Structure and Reactivity of Organic Ions in Gas-Phase Radiolysis. II. The Reactions of an Isopropyl Ion with Benzene and Toluene[1]

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Abstract: The gas-phase reactions of the isopropyl ion with benzene and toluene have been investigated by the γ radiolysis of propane–benzene–O_2 and propane–toluene–O_2 mixtures at room temperature. The maximum *G* values of isopropylbenzene and isopropyltoluene observed at very low concentrations of the aromatics (less than 1%) were in fair agreement with each other (1.06) and decreased with the concentration of the aromatics or, more significantly, with the addition of ammonia. The isomer distribution of isopropyltoluene was nearly in statistical ratio (44.2% *o*-, 40.4% *m*-, and 15.4% *p*-isopropyltoluene) at low pressure of toluene while the formation of the meta isomer became dominant (~60%) with increasing toluene pressure. In the competitive isopropylation of benzene and toluene under a variety of reaction conditions, a low positional and low substrate ($k_T/k_B = 0.6$–0.9) selectivity and also a low kinetic isotope effect in the isopropylation of benzene-d_6 were observed. The reaction mechanism was discussed in connection with high-pressure mass spectra and with liquid-phase isopropylation.

There has been much interest recently in ion–molecule reactions of aromatic compounds studied by high-pressure mass spectrometry[2–8] or gas-phase radiolysis.[1,9–11] The mass spectral results suggested that attachment of ions to aromatic molecules plays an important role in the gas-phase radiolysis of aromatic compounds. Ions produced in the gas phase exist as free ions and may react with aromatic molecules in the absence of interaction with solvent and counterions which is generally observed in the condensed-phase ionic reactions. Therefore, it is of particular interest to clarify the difference between the gas-phase and the condensed-phase reaction in order to understand the reaction mechanism in ionic organic chemistry, especially in connection with the mechanism of Friedel–Crafts alkylation discussed recently by Brown,[12] Olah,[13] and Nakane.[14]

In a previous paper of this series,[1] it has been shown that a $C_7H_7^+$ ion produced by the gas-phase radiolysis of toluene, ethylbenzene, and *m*-xylene reacts with respective aromatic molecules forming benzylated products. Of interest was the result indicating that electrophilic substitution of alkylbenzenes by free ions in the gas phase is thermodynamically controlled and predominantly leads to the formation of meta isomers though alkyl groups are ortho–para directing in electrophilic aromatic substitution. Thus, it appeared desirable to investigate further the scope and mechanism of this reaction in the simpler systems. The present paper describes the results obtained in the study of the gas-phase reaction of the $C_3H_7^+$ ion,

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[1] (a) Part I: Y. Yamamoto, S. Takamuku, and H. Sakurai, *J. Amer. Chem. Soc.*, **91**, 7192 (1969); (b) Y. Yamamoto, S. Takamuku, and H. Sakurai, *J. Phys. Chem.*, 74, 3325 (1970).

[2] L. I. Bone and J. H. Futrell, *J. Chem. Phys.*, 47, 4366 (1967).

[3] V. Aquilanti, A. Giardini-Guidoni, and G. G. Volpi, *Trans. Faraday Soc.*, **64**, 3282 (1968).

[4] F. H. Field, *J. Amer. Chem. Soc.*, **89**, 5328 (1967).

[5] M. S. B. Munson and F. H. Field, *ibid.*, **89**, 1047 (1967).

[6] S. Wexler and R. P. Clow, *ibid.*, **90**, 3940 (1968).

[7] S. Wexler and L. G. Pobo, *ibid.*, **91**, 7233 (1969).

[8] F. H. Field, P. Hamlet, and W. F. Libby, *ibid.*, **89**, 6035 (1967).

[9] S. G. Lias and P. Ausloos, *J. Chem. Phys.*, 37, 877 (1962).

[10] L. I. Bone, L. W. Sieck, and J. H. Futrell, *ibid.*, 44, 3667 (1966).

[11] F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, **89**, 6848 (1967).

[12] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 45 (1963).

[13] (a) G. A. Olah and N. A. Overchuk, *J. Amer. Chem. Soc.*, 87, 5786 (1965); (b) "Friedel–Crafts and Related Reactions," Vol. I–IV, G. A. Olah, Ed., Interscience, New York, N. Y., 1963–1965.

[14] R. Nakane, O. Kurihara, and A. Natsubori, *J. Amer. Chem. Soc.*, **91**, 4528 (1969).

produced by the γ irradiation of propane, with benzene and toluene.

Results and Discussion

The radiolytic and mass spectrometric investigations of propane have received fairly extensive attention and the behavior of propane under high-energy irradiation is now fairly well understood.[15,16] The high-pressure mass spectrum of propane[17] shows that fragment ions, such as $C_2H_5^+$, $C_2H_4^+$, and $C_2H_3^+$, produced in the primary act, react rapidly with propane by hydride ion abstraction.

$$R^+ + C_3H_8 \longrightarrow RH + C_3H_7^+ \qquad (1)$$

On the other hand, the $C_3H_7^+$ ion formed in both primary and secondary processes is relatively unreactive toward propane and at pressures greater than 0.14 mm, *ca.* 70% of all ions observed are the $C_3H_7^+$ ion which may be expected to undergo an electrophilic reaction with benzene and toluene added to the radiolytic systems of propane.

Isopropylation of Benzene. Mixtures of propane–benzene were irradiated with ^{60}Co γ-rays to a dose of 2.7×10^{19} eV at 100 mm of propane at room temperature. A radical scavenger (10 mol % of oxygen to propane) was present in all samples to prevent the product formation by neutral radicals. As shown in Figure 1, isopropylation of benzene was observed as a main reaction. Even at a very low concentration of benzene, a rapid isopropylation occurred. The G value (100 eV yield) of isopropylbenzene reached the maximum value of 1.06 and then gradually decreased with increasing partial pressure of benzene.[18] Ethylbenzene and *n*-propylbenzene were also produced as minor reaction products (shown in a ten times scale in Figure 1). It is known that a $C_3H_7^+$ ion formed in the primary fragmentation is nearly entirely the isopropyl ion, and the *n*-propyl ion is only formed by the reaction of a primary fragment ion, $C_2H_5^+$, with propane (reaction 1) to a limited amount. It can therefore be presumed that *n*-propylbenzene is produced by the reaction of the secondary $C_3H_7^+$ ions with benzene.[19] The pressure effect in Figure 1 seems to be partly explained by such a competition between benzene and propane for the primary $C_2H_5^+$ ions. The higher the concentration of benzene, the more primary $C_2H_5^+$ ions react with benzene leading to the formation of ethylbenzene resulting in the decrease in the yield of $C_3H_7^+$ ion *via* reaction 1, hence the yields of propylbenzenes. However, the increase in the yield of ethylbenzene observed was too small to account for the decrease of propylbenzenes. It appears that the intermediate ion produced by the addition of $C_3H_7^+$ ion to benzene may be sufficiently reactive to another benzene, leading to the formation of higher polymers, as suggested in the liquid-phase reaction.[20]

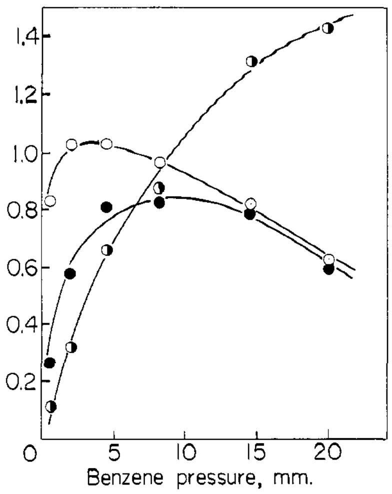

Figure 1. Variations of the yields of isopropylbenzene (○), *n*-propylbenzene (× 10, ●), and ethylbenzene (× 10, ◑) as a function of the benzene partial pressure in the radiolysis of C_3H_8 (100 mm)–O_2 (10 mm)–benzene mixtures.

On the basis of these experimental results together with those of mass spectra of propane, it is most reasonable to consider the isopropyl ion as the reactive species of the isopropylation. More conclusive evidence for the participation of the $C_3H_7^+$ ion was given by the experiments with added ammonia which is well known to react with $C_3H_7^+$ ion[21]

$$C_3H_7^+ + NH_3 \longrightarrow C_3H_6 + NH_4^+ \qquad (2)$$

The expected decrease in the yields of isopropylbenzene due to the competition between reaction 2 and the addition of the $C_3H_7^+$ ion to benzene was observed in a propane–benzene system, as shown in Figure 2, in which the results with isopropylation of toluene were also plotted.[22]

In agreement with these observations, Bone, Sieck, and Futrell[10] have shown that in the sensitized radiolysis of propane, benzene acts essentially as an ion scavenger and the $C_3H_7^+$ ion produced by γ irradiation is removed by reaction with benzene, though the addition products and the mode of the reaction were not investigated.

Isopropylation of Toluene. Isopropylations of toluene were carried out by the γ irradiation of propane–toluene–O_2 mixtures, similarly to those of benzene described above. The products were predominantly isomeric isopropyltoluenes as shown in Figure 3, in

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(15) G. G. Meisels in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley, New York, N. Y., 1968, p 347.

(16) G. R. Freeman, *Radiat. Res. Rev.*, **1**, 1 (1968).

(17) (a) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, 68, 3098 (1964); (b) K. R. Ryon and J. H. Futrell, *J. Chem. Phys.*, 42, 819 (1965); (c) L. I. Bone and J. H. Futrell, *ibid.*, **46**, 4084 (1967); (d) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, 41, 2998 (1964).

(18) The maximum value is rather small compared with the G value of $C_3H_7^+$ (~3.0), estimated from the mass spectrometry and the radiolysis of propane (ref 16). Even including the yield of *n*-propylbenzene, nearly two-thirds of the $C_3H_7^+$ ions seems to disappear by the following competing reactions as discussed later.

$$\begin{aligned} C_3H_7^+ + C_6H_6 &\longrightarrow [C_9H_{13}^+]^* \longrightarrow C_3H_6 + C_6H_7^+ \\ &\qquad\qquad\quad\ \longrightarrow C_9H_{13}^+ \\ C_9H_{13}^+ + C_6H_6 &\longrightarrow C_9H_{12}\,(\text{propylbenzenes}) + C_6H_7^+ \\ &\longrightarrow C_{15}H_{19}^+ \end{aligned}$$

(19) However, the structure of the $C_3H_7^+$ ion which gives *n*-propylbenzene is not clear because the *n*-propyl ion isomerizes quickly to the protonated cyclopropane structure [G. J. Karabatsos, C. E. Orzech, J. L. Frey, and S. Meyerson, *J. Amer. Chem. Soc.*, **92**, 606 (1970)].

(20) H. C. Brown and C. R. Smoot, *J. Amer. Chem. Soc.*, 78, 2176 (1956).

(21) (a) T. Miyazaki and S. Shida, *Bull. Chem. Soc. Jap.*, 38, 2114 (1965); (b) T. Miyazaki, *J. Phys. Chem.*, 71, 4282 (1967).

(22) These results did not satisfy the simple kinetic treatments to evaluate for relative rates of isopropyl ions with ammonia and with the aromatic molecules suggesting more complex effects of ammonia. One of the effects may be an enhancement of isopropylation by proton abstraction from intermediate benzenonium ions (discussed in the latter section) because of a strong proton affinity of ammonia.

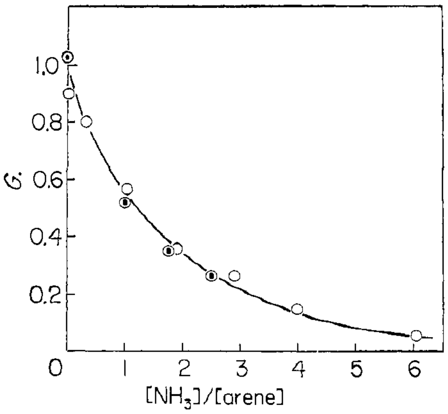

Figure 2. Variations of the yields of isopropylbenzene (◉) and isopropyltoluenes (○) as a function of the ammonia concentration in the radiolysis of C_3H_8 (100 mm)-O_2 (10 mm)-benzene (5 mm)-NH_3 and C_3H_8 (100 mm)-O_2 (10 mm)-toluene (5 mm)-NH_3, respectively.

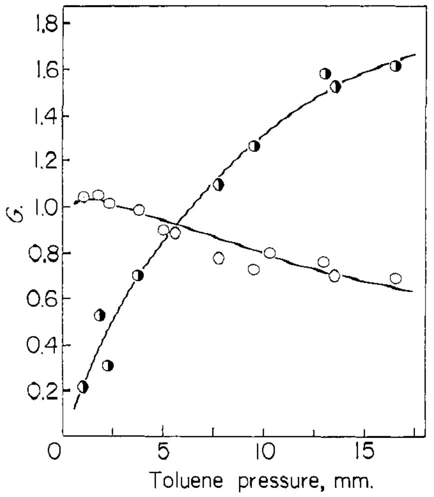

Figure 3. Variations of the yields of isopropyltoluenes (○) and ethyltoluene (× 10, ◑) as a function of the toluene partial pressure in the radiolysis of C_3H_8 (100 mm)-O_2 (10 mm)-toluene mixtures.

which the minor products (*n*-propyltoluenes) are not indicated. The maximum G value of total isopropyltoluenes was the same as that of isopropylbenzene (1.06). Consistency in the yield of isopropylation and similarity in the effects of aromatic partial pressure and also added ammonia in both systems suggest the similar reaction mechanism operating in the both propane-benzene and propane-toluene systems.

Of particular interest with the reaction mechanism is the orientation in the isopropylation of toluene in the gas phase. The isomer distributions of the isopropyltoluene as a function of the partial pressure of toluene are shown in Figure 4. The distribution observed at 1.8 mm of toluene was 44.2% ortho, 40.4% meta, and 15.4% para isomer which is nearly equal to the statistical ratio (4:4:2). However, the amount of ortho and para isomer substantially decreased with increasing the toluene pressure, resulting in a change of the isomer distribution to 28.2% ortho, 59.2% meta, and 12.6% para isomer at 16.6 mm of toluene. Compared to the liquid-phase Friedel-Crafts isopropylation of toluene (44-60% ortho, 14-18% meta, and 25-40% para isomer),[13,23] the formation of large amounts of meta

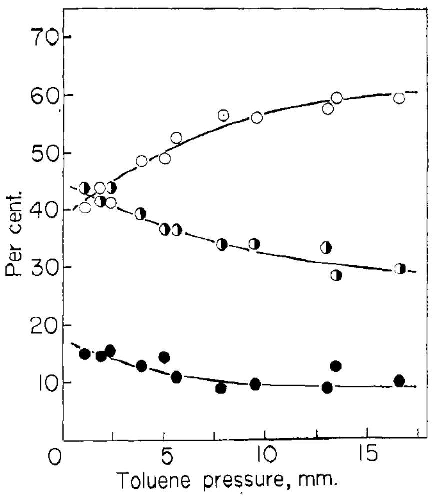

Figure 4. Variations of the distribution of isomeric isopropyltoluene as a function of the toluene partial pressure in the radiolysis of C_3H_8 (100 mm)-O_2 (10 mm)-toluene mixtures: ◑, *o*-; ○, *m*-; and ●, *p*-isopropyltoluene.

isomer was characteristic of the gas-phase isopropylation. Thus, the quite low positional selectivity (intramolecular) was observed at lower pressures of toluene while the distribution of meta isomer became dominant at higher pressure of toluene.

Competitive Isopropylation of Benzene and Toluene, and Kinetic Isotope Effect. Concerning a very low positional selectivity observed in the gas-phase isopropylation, it seemed to be desirable to determine the substrate selectivity (intermolecular), *i.e.*, the relative reactivities of isopropyl ion to toluene and benzene (k_T/k_B). For this purpose, benzene-toluene mixtures were irradiated in the presence of propane (100 mm) containing 10 mol % oxygen, and the yields of isopropylbenzene and isopropyltoluenes were determined by gas chromatographic analysis. The results are summarized in Table I, together with those of the kinetic isotope effects (k_H/k_D) in the competitive isopropylation of benzene-benzene-d_6.

Interconnecting to the low positional selectivity of isopropylation of toluene in the gas phase, a very low substrate selectivity (k_T/k_B = 0.6-0.9) was also observed. Though the ratio slightly depends on the molar ratio of toluene and benzene, the trend, *i.e.*, benzene is more reactive than toluene, seems to be reasonable. Such a low selectivity is consistent with the fact that the $C_2D_5^+$ ion is more reactive with benzene than with toluene in the gas-phase radiolysis of propane as reported by Lias and Ausloos, who did not investigate the mode of reaction.[9,24] In the liquid-phase reaction, similar low substrate selectivities were re-

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(23) G. A. Olah, S. H. Flood, S. J. Kuhn, M. E. Moffatt, and N. A. Overchuk, *J. Amer. Chem. Soc.*, **86**, 1046 (1964).

(24) Lias and Ausloos suggested that $C_2D_5^+$ ion produced in the gas-phase radiolysis of C_3D_8 abstracts D^- from C_3D_8 or adds to an aromatic molecule, where RH shows olefinic or aromatic compound

$$C_2D_5^+ + C_3D_8 \xrightarrow{k_1} C_2D_6 + C_3D_7^+$$

$$C_2D_5^+ + RH \xrightarrow{k_2} C_2D_5RH^+ \longrightarrow \text{products other than } C_2D_5H$$

By the determination of isotopic ethanes they obtained approximate values of k_2/k_1, which were 4.15 and 5.1 for toluene and benzene, respectively, showing the relative reactivity ratio, k_T/k_B = 0.81.

Table I. Competitive Isopropylation of Benzene and Toluene, and Kinetic Isotope Effect to Benzene-d_6[a]

Toluene, mm	Benzene, mm	[Toluene]/[benzene]	k_T/k_B	k_H/k_D	Isomer distribution of isopropyltoluene, % Ortho	Meta	Para
2.0	2.2	0.91	0.86	0.91	42.0	44.0	14.0
2.0	2.3^b	0.87^b	0.78^b		40.5	44.7	14.8
4.8	5.2	0.92	0.69	1.04	35.2	53.6	11.2
4.7	5.0^b	0.94^b	0.72^b		36.0	52.0	12.0
2.0	8.0	0.25	0.63	1.10	36.1	50.0	13.9
2.0	8.0^b	0.25^b	0.69^b				
10.0	10.6	0.94	0.65	1.34	31.0	56.5	12.5
10.0	10.2^b	0.98^b	0.87^b		35.1	52.8	12.1

[a] Isopropylations were carried out by γ irradiation of C_3H_8–O_2 (100:10) containing different amounts of aromatics to a dose of 2.7×10^{19} eV. [b] Benzene-d_6 was used instead of benzene-h_6.

cently reported by Nakane, Kurihara, and Natsubori.[14] In Friedel–Crafts ethylations of benzene and toluene in nonpolar organic solvent (such as n-hexane) in which ethyl fluoride can be ionized directly to the ethyl carbonium ion in the presence of boron fluoride, an anomalous substrate selectivity ($k_T/k_B = 0.61$) was obtained though the isomer distribution of ethyltoluene was not statistical: 49.2% ortho, 27.1% meta, and 23.7% para isomer. Similar results were also obtained in the Friedel–Crafts isopropylation in n-hexane.[25]

The kinetic isotope effect (k_H/k_D) which gives important information about the transition state of the isopropylation was determined from competition of toluene–benzene and toluene–benzene-d_6 at various reaction conditions as shown in Table I. Only small isotope effects were observed though the reactivity ratio slightly depended on the composition of aromatics. It seems that the ratio increases with the total pressure of aromatics. A small inverse kinetic isotope effect[26] found at low pressure of aromatics may be caused by the fact that the initial sp^2 C–H bond may easily change to sp^3 bonding by the attack of carbonium ion in heavier molecules as suggested by Olah[27] and Dolbier.[28]

At any rate, the absence of a large kinetic isotope effect observed seems to indicate that the proton abstraction from the intermediate in the thermal equilibrated state is not a rate-determining step in the present isopropylation, at least at the low concentration of aromatics.

Aspects of Reaction Mechanism. Recently, a considerable amount of information has been obtained concerning the ion–molecule reactions of aromatic hydrocarbon, mainly through investigations by mass spectrometry. Of interest, in connection with the present work, is the study on the reaction of principal primary ions from propane, $C_3H_8^+$, $C_3H_7^+$, etc., with benzene carried out by Bone and Futrell using a tandem mass spectrometer.[2] For a parent ion of propane, two modes of reaction were observed, though the proton transfer reaction 4 was only 3% of the charge exchange reaction 3. On the basis of these observations, the

$$C_3H_8^+ + C_6H_6 \longrightarrow C_3H_8 + C_6H_6^+ \tag{3}$$

$$C_3H_8^+ + C_6H_6 \longrightarrow C_3H_7\cdot + C_6H_7^+ \tag{4}$$

contribution of the parent ion, which comprises 10% of the total ion, to the isopropylation of aromatics can be ignored.

On the other hand, the reactions of $C_3H_7^+$ ion with benzene, which are instructive for the present isopropylation, were also studied in more detail and the results were understood in terms of the reaction sequence

$$C_3H_7^+ + C_6H_6 \longrightarrow [C_9H_{13}^+]^* \tag{5}$$

$$[C_9H_{13}^+]^* \longrightarrow C_3H_6 + C_6H_7^+ \tag{6}$$

$$[C_9H_{13}^+]^* + C_6H_6 \longrightarrow C_9H_{13}^+ + C_6H_6 \tag{7}$$

Here, brackets with an asterisk denote a collision complex which will dissociate, unless stabilized. As to these carbonium ions, different from the parent ion, a charge exchange with benzene is an energetically unfavorable process because the ionization potential of C_3H_7 radical (7.90 eV) is less than that of benzene (9.24 eV). Furthermore, the most prominent reaction observed in the high-pressure mass spectra of pure benzene[6] and toluene[6,29] was the condensation of $C_6H_6^+$ ion with a benzene molecule and $C_7H_7^+$ and $C_7H_8^+$ ions with a toluene molecule, respectively. In addition, Field[8,30] showed that the ions R^+ ($C_6H_6^+$, $C_3H_3^+$, and $C_9H_7^+$) produced from benzene were present in an equilibrium state with the adduct ions, as[31]

$$R^+ + C_6H_6 \rightleftarrows [C_6H_6R^+]^* \tag{8}$$

$$[C_6H_6R^+]^* + C_6H_6 \longrightarrow C_6H_6R^+ + C_6H_6 \tag{9}$$

As a whole, the investigations cited above provide a consistent and satisfactory picture of the initial pro-

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(25) R. Nakane, *Nippon Kagaku Zasshi*, **90**, 17 (1969).

(26) Recently, Lifshitz and Reuben have observed similar inverse isotope effects for the condensation of $C_6H_5^+$ with C_6H_6 forming $C_{12}H_{11}^+$ ion by the mass spectrometric investigation of benzene and benzene-d_6 using a pulsed ion source ($k_D/k_H = 1.44$), while in most other reactions involving the production of H or H_2, the ratio k_D/k_H was much smaller. Since for reaction a, an isotope effect of 1.04 only is

$$C_6H_5^+ + C_6H_6 \underset{b}{\overset{a}{\rightleftarrows}} C_{12}H_{11}^+ \xrightarrow{c} C_6H_5 + C_6H_6^+$$

$$\xrightarrow{d} C_{12}H_9^+ + H_2$$

$$\xrightarrow{e} C_{10}H_9^+ + C_2H_2$$

expected theoretically, the formation of a long-lived intermediate ($C_{12}H_{11}^+$) has been assumed, and competing unimolecular reactions (b–e), on which a normal secondary isotope effect (reaction b, c, and e) and a normal primary isotope effect (reaction d) are expected [C. Lifshitz and B. G. Reuben, *J. Chem. Phys.*, **50**, 951 (1969)]. However, the bimolecular reactions of the long-lived intermediate, which were assumed in the present investigation, were not clear because of the low pressure in the mass spectrometer (1–5 × 10^{-4} mm).

(27) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, **84**, 1688 (1962).

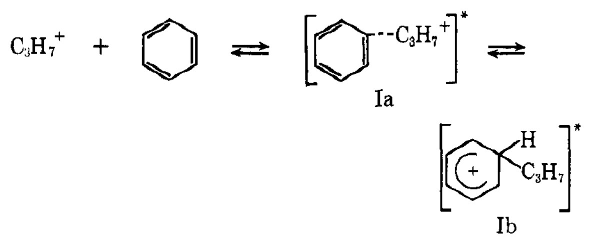
(28) W. R. Dolbier, Jr., and S.-H. Dai, *ibid.*, **90**, 5028 (1968).

(29) A. Giardini-Guidoni and F. Zocchi, *Trans. Faraday Soc.*, **64**, 2342 (1968).

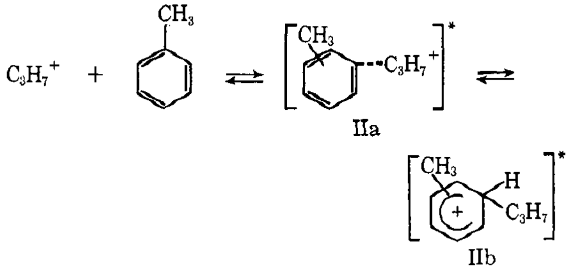
(30) F. H. Field, P. Hamlet, and W. F. Libby, *J. Amer. Chem. Soc.*, **91**, 2839 (1969).

(31) The further mechanistic investigation was carried out by S. Wexler and L. G. Pobo, *J. Phys. Chem.*, **74**, 257 (1970).

cesses in the gas-phase electrophilic aromatic substitution. It is, therefore, suggested that in the gas-phase isopropylation of benzene and toluene, the excited complex formed initially must be an energetic π complex (I_a and II_a) where the incoming isopropyl ion is loosely bound to the aromatic ring at a particular carbon atom because the relative rate of toluene to benzene was smaller than 1 and close to the statistical ratio (5:6). This π complex would be transformed



(10)



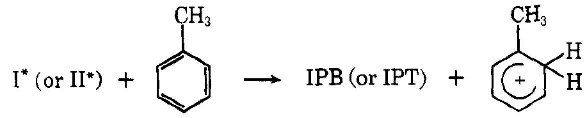
(11)

into a σ complex unimolecularly in the gas phase. Since the free $C_3H_7^+$ ion is a strong electrophile in the gas phase, the selectivity of the $C_3H_7^+$ ion may be considered to be very small as suggested by Brown.[12] Then, the statistical distribution among these complexes is expected: I:II = 6:5 and o-II:*m*-II:*p*-II = 2:2:1.

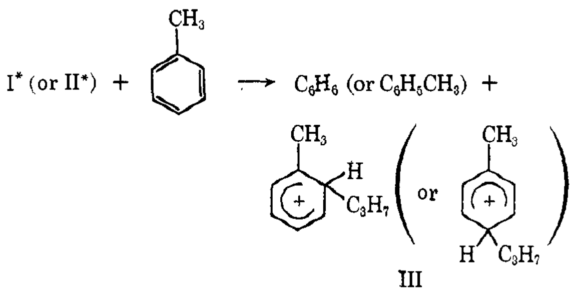
The effects (the statistical distribution at low aromatic concentration going to thermodynamically controlled distribution at high concentration; increasing isotope effect with increasing the concentration) seem to suggest a competition between two mechanisms, one fast, the other slow. The fast reaction (12) occurring at low aromatic concentration may be caused by the fast proton acceptor (S) which could possibly be olefins (C_3H_6, C_2H_4) produced by the radiolysis of propane and/or oxygenated products (H_2O, ROH, etc.) from added oxygen because of their large proton affinities.

$$I^* \text{ (or } II^*) + S \longrightarrow \text{IPB (or IPT)} + SH^+ \qquad (12)$$

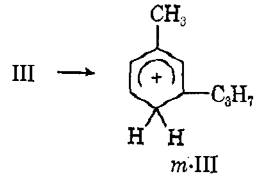
Since I* and II* are excited enough to make this reaction sufficiently exothermic and also very fast, one would expect a statistical product distribution and a small kinetic isotope effect. Increasing the concentration of aromatics, interaction of I* (or II*) with aromatics in which two modes of reaction may be expected becomes significant. Reaction 13 may produce isopropyltoluenes in a similar isomer distribution to that of reaction 12, while in reaction 14, I* (or II*) might act as a less electrophilic reagent for another toluene molecule and produce a less energetic complex (III), which may correspond to the collisional deactivation (reaction 7 or 9) observed in the high-pressure mass spectra. The complex III thus formed may be a stable σ complex which is similar to that proposed previously in the benzylation[1] and expected to isomerize to the most stable meta isomer (*m*-III) of the possible isomeric benzenonium ions. Such an isomerization is thought to occur easily in the gas phase where benzenonium ions exist as free ions with appropriate vibrational energy, and hence the further reactions become thermodynamically controlled. The



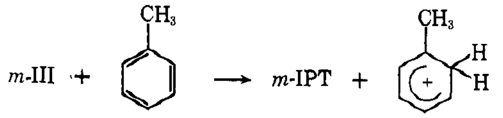
(13)



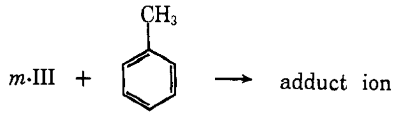
(14)



(15)



(16)



(17)

intermediate *m*-III may subject to a proton transfer to toluene (reaction 16) forming preferentially *m*-isopropyltoluene or add to another toluene giving a high-polymeric ion (reaction 17). The less energetic the intermediate, the greater the tendency for the addition reaction because reaction 16 is somewhat endothermic.

In the gas-phase radiolysis of hydrocarbons, the charge neutralization is known to occur between electrons and relatively long-lived positive ions leading to the formation of the vibrationally excited molecules which may dissociate to stable species. Ions which appear after a series of rapid ion–molecule reactions may undergo the neutralization because the ion–molecule reactions are often very rapid and occur with collision efficiency.[15] In the present situation, *m*-III, in addition to the polymeric ions, may be involved in the neutralization

$$m\text{-III} + e^- \longrightarrow m\text{-IPT} + H \qquad (18)$$

However, in the previous investigation[1] on an electrophilic substitution of toluene with $C_7H_7^+$ ion, the yield of benzylated toluene was not appreciably affected by the addition of an electron scavenger (N_2O). Therefore, it seems that a neutralization process does not play an important role in the substitution reaction of aromatic compounds.

Experimental Section

Materials. Benzene and toluene obtained from Wako Pure Chemical Industrial Co. were fractionated through a spinningband column after the usual purification. The purity determined gas chromatographically was more than 99.9%. Propane obtained from Takachiho Shoji Co. was purified by several trap-to-trap distillations through a sodium mirror and stored in a storage bulb. Oxygen obtained from Awao Industrial Co. was dried by a P_2O_5 column and was used without further purification. Benzene-d_6 purchased from Merk Co., Germany, was also used without purification except drying by a sodium mirror (deuterium content, 99.5%).

Procedures. The experimental procedures were similar to those reported previously.[1] The irradiation cells were Pyrex cylinders of approximately 120 ml in volume with a break-seal. After the cells were evacuated at a pressure of 10^{-6} mm Hg overnight, the propane vapor from the storage bulb was dried by passing through a sodium mirror, and then introduced into the cells at a pressure of 100 mm. The pressure of the sample was measured by a mercury manometer. Then, a known amount of benzene or toluene, dried similarly, was introduced to the cells, in which propane was already condensed at −196°, by a trap-to-trap distillation from a cell for sampling. Finally, oxygen was introduced into the cell through a P_2O_5 column and the cells were sealed.

Samples were irradiated with γ rays from a 5000-Ci ^{60}Co source at room temperature. The dose rate to propane was determined by a ethylene dosimetry, using a G value of 1.28 for hydrogen formation[32] and correcting for the electron density of propane relative to ethylene. The irradiations were carried out at a constant dose rate of 1.85×10^{15} eV/hr μmol for propane. The G values of the product were calculated on the energy absorbed by propane alone.

After irradiation, the cell was sealed to a high vacuum line and the break-seal was ruptured after evacuation. The gases volatile at −120° (mainly propane and oxygen) were pumped off through a spiral trap kept at −120° and then the residual liquid fraction was collected into a capillary glass tube and analyzed by gas chromatographic comparison with authentic samples using several columns (Apiezon L, 6 m at 100 or 130° and Benton 34, 3 m + Apiezon L, 3 m at 130°). The yields of the products were determined by comparison of peak areas with those of known amounts of benzene, which were submitted to gas chromatography before each analysis. The calibration of the sensitivity for a flame-ionization detector was also carried out.

Competitive isopropylations of benzene and toluene or benzene-d_6 and toluene were also carried out similarly to those described above using benzene–toluene mixtures.

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Cation–Anion Combination Reactions. II.[1] The Reactions of *p*-Nitrobenzenediazonium Ion with Hydroxide Ion in Aqueous Solution

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Abstract: The reaction of *p*-nitrobenzenediazonium ion with hydroxide ion in aqueous solution produces the *syn*-diazotate in a fast second-order reaction. The *syn*-diazotate slowly rearranges to the more stable *anti*-diazotate in a first-order process. The rate and equilibrium constants for the individual steps are evaluated and the previously proposed mechanism for the reaction is modified in several particulars.

In earlier work,[1] we noted the peculiar reactivity order $N_3^- > CH_3O^- > CN^-$ for the rates of reactions of malachite green derivatives in methanol solution. The order of azide faster than cyanide was found to be independent of solvent in methanol, dimethylformamide, and dimethyl sulfoxide. The rate order is the exact opposite of the equilibrium order for these reactions. The further observation that these nucleophiles follow the Brønsted order $CN^- > N_3^-$ in proton transfer reactions in DMSO indicates that the order for the malachite green reactions is not a characteristic of either the anions or of any solvent.

In other studies in these laboratories, attempts to measure rate and equilibrium constants for reactions of malachite green with other nucleophiles in DMSO solution have been thwarted either by rates too fast to measure (for example, thiophenoxide ion) or by unfavorable equilibria (acetate, chloride, *p*-nitrophenoxide).

Our curiosity about these reactions was heightened after a literature search failed to reveal any other reaction in which azide ion reacts faster than cyanide ion in a nucleophilic attack. On the basis of Edwards' parameters for these two anions,[2] it does not appear that any combination of basicity and polarizability could give the observed order.

It appeared to us that the one feature of the malachite green reactions which differs drastically from other reactions which have been studied is that the anions are reacting directly with a rather nonspecifically solvated cation without the necessity of displacing any leaving group. In order to check this hypothesis, we have sought other reactions which would have this feature, but be as different from malachite green reactions as possible in other respects.

Various substituted benzenediazonium ions are known to undergo reactions of the desired type, and some rate and equilibrium data are available for these

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(1) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, 89, 2063 (1967), is to be considered as paper I of the present series. We gratefully acknowledge support of this work by National Institutes of Health, Grant GM-12832.

(2) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 84, 16 (1962). For a tabulation of parameters, see J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 253.