

Several experiments indicate that benzenesulfonates and bromobenzenesulfonates are also readily cleaved to alkoxides by sodium naphthalene, but that a competing reaction, reduction of the alkyl group to alkane, becomes important in the case of methanesulfonates. Similar results have been reported by Cram and Dalton for the reaction of methanesulfonates with potassium in ether solvents.¹¹ In related studies preliminary experiments indicate sodium naphthalene to be an excellent agent for the reductive cleavage of toluenesulfonamides. This, and more detailed discussions of the mechanism and scope of the toluenesulfonate cleavage reaction, will be dealt with in future articles.

(11) D. J. Cram and C. K. Dalton, *J. Am. Chem. Soc.*, **85**, 1268 (1963).

(12) Address correspondence to the Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203.

W. D. Closson,¹² Peter Wriede

Department of Chemistry, Columbia University
New York, New York 10027

Shelton Bank

Esso Research and Engineering Co.
Linden, New Jersey 07036

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Ion-Molecule Reactions in the Liquid and Solid Phase Radiolysis of Hydrocarbon Mixtures¹

Sir:

The spectrophotometric observations of cations and anions by Hamill and co-workers² have conclusively demonstrated that, in hydrocarbon glasses, cations may take part in ion-molecule reactions prior to recombination with a negatively charged species. Furthermore, Freeman and Fayadh³ have noted that, in the liquid phase, most ion pairs undergo recombination in a period of $10^{-10\pm 1}$ sec, and therefore they concluded that there may be sufficient time for ionic processes to occur.

Although it is thus well established that fast ion-molecule reactions can occur in both liquid and solid phase radiolysis of hydrocarbons, it has not until now been possible to unambiguously identify a particular stable product formed in the radiolysis of pure hydrocarbons or hydrocarbon mixtures as originating from a well-defined ion-molecule reaction. The occurrence of proton-transfer reactions involving the parent ion has occasionally been suggested, but the importance of such a reaction is difficult to establish, because the resulting products are usually not clearly distinguishable from those produced by free-radical reactions involving thermal or hot H atoms.

In recent years, progress has been made toward a better understanding of ion-molecule reactions occurring in the gas-phase radiolysis of hydrocarbons.⁴ It was, therefore, considered timely to initiate similar systematic investigations of ion-molecule reactions occurring in

(1) This research was supported by the U. S. Atomic Energy Commission.

(2) See, for instance, (a) P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 500 (1962); (b) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *ibid.*, **84**, 4230 (1962); (c) J. P. Guarino and W. H. Hamill, *ibid.*, **86**, 777 (1964).

(3) G. R. Freeman and J. M. Fayadh, *J. Chem. Phys.*, **43**, 86 (1965).

(4) (a) I. B. Sandoval and P. J. Ausloos, *ibid.*, **38**, 2454 (1963); (b) R. P. Borkowski and P. Ausloos, *ibid.*, **40**, 1128 (1964); (c) P. Ausloos and S. G. Lias, *ibid.*, **40**, 3599 (1964); (d) *ibid.*, **43**, 127 (1965); (e) *Discussions Faraday Soc.*, No. 39, 36 (1965).

the liquid and solid phase radiolysis. Because in the condensed phase fragmentation of the parent ion will occur to a much lesser extent than in the gas phase,⁵ the parent ion will play a major role in the ionic reaction mechanism. In the gas phase radiolysis^{4d} and photoionization⁶ of alkanes, exothermic H₂-transfer reactions from the parent ion to cyclopropane or to a lower olefin such as propylene have been shown to



occur even when these additives constitute only 1% of the total reaction mixture. If the distinctive propane products formed in these reactions are observed in the liquid and solid phase radiolysis of these systems, then their presence would constitute unambiguous proof that the parent ion can indeed undergo ion-molecule reactions in the condensed phase. In addition, variations in the yield of this product would provide information about the number of parent ions which could undergo reaction in competition with other processes such as neutralization under various experimental conditions. The following rather striking experimental observations show that ion-molecule reactions involving the parent ion indeed occur with high efficiency in the liquid and solid phase radiolysis.

1. Addition of 5 mole % of cyclo-C₃D₆ to perprotonated *n*-pentane, isopentane, *n*-hexane, or 3-methylpentane results in the formation of CD₂HCD₂CD₂H as a major product [*G* (molecules per 100 ev) = 0.5–1.0] with the exclusion of any significant amount of other deuterated propanes. *G*(CD₂HCD₂CD₂H) does not vary by more than 20% when the temperature is varied from 77 to 300°K. An increase in the concentration of cyclo-C₃D₆ from 1 to 10 mole % raises *G*(CD₂HCD₂CD₂H) by 50% at most. On the other hand, addition of 1 mole % of CCl₄ increases the value of *G*(CD₂HCD₂CD₂H) to 2.5, both at 77 and 193°K. The latter value is independent of the concentration of cyclo-C₃D₆. This result is consistent with the spectrophotometric observations of Guarino and Hamill,^{2c} which demonstrate that CCl₄ is an excellent electron trap whose addition to a hydrocarbon should increase the chances that the parent ion will react prior to neutralization.

2. In order to determine if, in the experiments mentioned above, CD₂HCD₂CD₂H is indeed formed by an H₂-transfer reaction rather than by two consecutive H-atom transfer processes, 1 mole % of cyclo-C₃D₆ was added to an equimolar *i*-C₅H₁₂-*i*-C₅D₁₂ mixture containing 1 mole % CCl₄. Mass spectrometric analysis of the propane which was formed with a *G* value of 2.2 was as follows: CD₃CD₂CD₃, 40%; CD₃CD₂CD₂H, 5%; CD₂HCD₂CD₂H, 50%; (C₃D₃H₃ + C₃D₄H₄ + C₃D₅H₅ + C₃D₂H₆), <1%; (C₃D₁H₇ + C₃H₈), ~5%. The observed propane composition clearly demonstrates that the large majority of the propane is indeed formed by a one-step reaction involving the transfer of a hydrogen molecule to cyclopropane. Similar isotopic analyses were obtained when equimolar *n*-C₄H₁₀-*n*-C₄D₁₀ mixtures, or *n*-C₅H₁₂-*n*-C₅D₁₂ mixtures, were irradiated in the presence of cyclo-C₃D₆.

(5) (a) P. Ausloos and S. G. Lias, *ibid.*, No. 36, 66 (1963); (b) A. Scala, S. G. Lias, and P. Ausloos, to be published.

(6) (a) R. D. Doepker, and P. Ausloos, *J. Chem. Phys.*, **42**, 3746 (1965); (b) P. Ausloos and S. G. Lias, to be published.

3. When propylene- d_6 , instead of cyclopropane- d_6 , is added to $n\text{-C}_5\text{H}_{12}$ or $i\text{-C}_5\text{H}_{12}$, propane- d_6 appears again as a major product, but from the mass spectrum it was seen that, in agreement with observations made in analogous gas phase systems,^{4d} the propane- d_6 has the structure $\text{CD}_3\text{CDHCD}_2\text{H}$. Mass spectrometric analysis of the propane fraction (C_3D_8 , 45%; $\text{C}_3\text{D}_7\text{H}$, 10%; $\text{CD}_3\text{CDHCD}_2\text{H}$, 45%) formed in the radiolysis of a $n\text{-C}_5\text{H}_{12}\text{-}n\text{-C}_5\text{D}_{12}\text{-CD}_3\text{CDCD}_2\text{-CCl}_4$ (1:1:0.01:0.01) mixture at 193°K indicates that the majority of the propane must also be produced by an H_2 -transfer reaction. Addition of a free-radical scavenger such as oxygen reduces the yield of $\text{C}_3\text{D}_7\text{H}$ relative to the yields of C_3D_8 and $\text{CD}_3\text{CDHCD}_2\text{H}$.

4. H_2 -transfer reactions to other unsaturates such as C_2D_2 , C_2D_4 , and $\text{CD}_3\text{CD}_2\text{CDCD}_2$ have also been noted to occur with high efficiency. For instance, $\text{CD}_2\text{HCD}_2\text{H}$ is formed with a G value of 2 when a $\text{C}_5\text{H}_{12}\text{-CCl}_4$ (1:0.03) mixture is irradiated in the presence of C_2D_4 . Furthermore, the isotopic composition of the ethane fraction [$G(\text{ethane}) = 1.5$] produced in the radiolysis of a $i\text{-C}_5\text{H}_{12}\text{-}i\text{-C}_5\text{D}_{12}\text{-C}_2\text{D}_4\text{-CCl}_4$ (1:1:0.03:0.03) mixture, in the presence of oxygen at 193°K, is as follows: C_2D_6 , 43%; $\text{C}_2\text{D}_5\text{H}$, 2%; $\text{CD}_2\text{HCD}_2\text{H}$, 48%; C_2H_6 , 7%.

Besides confirming² the important role ion-molecule reactions can play in the condensed phase, the experimental observations reported above demonstrate that it is feasible to carry out systematic quantitative studies of specific ion-molecule reactions in the liquid and solid phases. The results reported here also indicate that the reactions of the parent ion which occur in the gas phase may be expected to take place with comparable efficiency in the condensed phase. It is, furthermore, of particular interest to point out that the present observations imply that, in the condensed phase radiolysis of larger pure alkanes, reaction of the parent ion with neighboring molecules must be slow and may actually not occur prior to neutralization. This conclusion is consistent with the gas phase radiolysis data,^{4d} as well as with the interpretations put forward in a number of recent liquid phase studies.⁷⁻⁹

A detailed report on ion-molecule reactions occurring in the liquid and solid phase is forthcoming.

(7) S. Z. Toma and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 4761 (1964).

(8) P. J. Dyne, *Can. J. Chem.*, **43**, 1080 (1965).

(9) G. Meissner and A. Henglein, *Ber. Bunsenges. Physik. Chem.*, **69**, 264 (1965).

P. Ausloos, A. A. Scala, S. G. Lias
National Bureau of Standards
Washington, D. C. 20234
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Oxidation by Molecular Oxygen. III. Oxidation of Saturated Hydrocarbons by an Intermediate in the Reaction of Some Carbenes with Oxygen¹⁻³

Sir:

In a continuation of our studies on oxidations by molecular oxygen, and on possible oxygen atom transfer reactions,³ we have found that saturated hydrocarbons

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(3) Part II: G. A. Hamilton, *J. Am. Chem. Soc.*, **86**, 3391 (1964).

are oxidized at room temperature when some carbenes are generated in oxygen-saturated hydrocarbon solvents.⁴ As shown in Table I, extensive oxidation of the hydrocarbon solvent occurs when the carbene source is diazofluorene or diphenyldiazomethane but not when it is diethyl diazomalonate or diazocyclopentadiene. Under the same conditions fluorenone induced no oxidation of the solvent and benzophenone led to the formation of ketone and alcohol in a much different ratio than that observed when diphenyldiazomethane was used. Thus, the solvent oxidation is not due to a light reaction involving the ketone derived from the diazo compound; it is probably due to the reaction of oxygen with some intermediate in the photodecomposition reaction. Control experiments indicate that cyclohexanone is not formed by further oxidation of cyclohexanol but must be formed directly from some intermediate in the reaction.

Table I. The Oxidized Products Obtained from the Photodecomposition of Various Diazo Compounds in Oxygen-Saturated Cyclohexane Solutions^a

Diazo compd or catalyst	Irradiation time, min	Cyclohexanol yield, ^b %	Cyclohexanone yield, ^b %	Yield of ketone from diazo compd, ^b %
Diazofluorene	300	29	19	55
	125	29	22	...
None	300	<1	<1	...
Fluorenone	300	<1	<1	...
Diphenyldiazomethane	6.3	5.7	2.0	37
	20	10.5	3.6	...
	47	15	6.8	...
	88	21	13	80
Benzophenone	7	1.2	2.4	101
	28	6.3	10.5	104
	52	11	18	101
	71	18	25	100
$\text{N}_2\text{C}(\text{CO}_2\text{Et})_2$	300	<1	<1	...
Diazocyclopentadiene	300	ca. 1	ca. 0.7	...

^a In all experiments oxygen was continuously bubbled through the solutions contained in Pyrex, maintained at 25°, and irradiated with a sun lamp. As shown by infrared spectra diazofluorene, diethyl diazomalonate, and diazocyclopentadiene completely react in 2-4 hr and diphenyldiazomethane in less than 1 hr. ^b Assayed by gas chromatography; yields based on the initial amounts of the diazo compounds or ketone catalysts.

The reactivity of the diazofluorene-oxygen system toward primary, secondary, and tertiary hydrogens was determined from the yield of alcohols obtained following lithium aluminum hydride reduction of the products from the oxidation of 2-methylbutane and adamantane. With 2-methylbutane the relative reactivity per hydrogen is: primary, (1); secondary, 15; tertiary, 140. With adamantane it is: secondary, (1); tertiary, 10. The selectivity is somewhat reminiscent of radical reactions although it is greater than that shown by most radical species.⁵ In order to distinguish between a hydrogen abstraction and an insertion mechanism for the oxidation, *cis*- and *trans*-1,2-dimethylcyclohexane were oxidized separately by the diazofluorene-oxygen system. Both hydrocarbons give

(4) Under the same conditions aromatic solvents give low yields of phenols (1-3%), and olefinic solvents give a large number of products which have not been investigated further.

(5) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).