

the only change required would be a modification of eq. 18 into the form

$$\partial \Delta F_{\text{ex}} / \partial \alpha = \epsilon \cdot 3RT(\alpha - \alpha^{-1}) / \mathcal{R} \quad (41)$$

where the factor ϵ , equal to unity in the absence of cross links and greater than unity when they are present, is introduced to take into account the lesser extensibility of a cross-linked chain; the sole result of this is to replace Γ by Γ/ϵ , and hence to increase the slope (by a factor of $\epsilon^{0.5}$), which is consistent with what is observed; on this basis ϵ would be 7 for biphenyl-4-carboxylate and 15 for 3-phenanthroate.

Considering next the ratio $S/I\zeta_0$ for the lines, from eq. 39 we would expect it to be equal to the value of K for the particular cosolute; Table I shows that this is not so, but that the values of $S/I\zeta_0$ differ from K by an amount which is fairly constant at about $30 M^{-1}$. (It may seem somewhat arbitrary to use ζ_0 (*i.e.*, that for $a = 0$, as given in footnote 7) here in place of any other values of ζ , but since the plots are linear they must hold down to $a = 0$, and additionally most of the approximations made in the theoretical treatment, as to activity coefficients, etc., become completely valid at $a = 0$.)

This situation is puzzling, since the agreement with theory up to this stage, *i.e.*, the linearity of the plots in Fig. 1 and the essential agreement between their slopes and the expected value, suggests that the broad outline of the present treatment is correct; further, if we trace back the source for the identification of $S/I\zeta_0$ with K , we find that it derives directly from the formulation in eq. 1 of the anion binding (the counter-ion term being now completely neglected), and the assumptions of the statistical thermodynamic part of the treatment are not directly involved.

One possible explanation of the discrepancy is that the bound anions are not fixed on definite sites, but are

free to move along the chain while still attached to it; P. M. has shown⁹ that if this *adsorbate mobility* is complete, then for small degrees of coverage the system obeys the Langmuir isotherm but the apparent binding constant obtained (*i.e.*, from dialysis) is twice its correct value; however, this would involve a constant *multiplicative* factor, rather than the constant *additive* factor that the present case requires; additionally, such mobility would lead to a similar twofold error in the site size, n , whereas the essential agreement between the predicted and the experimental slopes suggests that our experimental n -value (*i.e.* that from dialysis) is correct.

Alternatively, since what is observed is a lowering in the effective value of K for expansion as compared with that from dialysis, it is possible that some other type of counter-ion binding (*i.e.*, not expressed by a Langmuir-type formulation with binding constant K') is involved; for *any* form of counter-ion binding must reduce the free ionic excess, through converting bound anions into bound ion-pairs (assumedly inactive in changing the volume of the coil); this could readily be checked by using, say, lithium or potassium as the counter-ion in place of sodium.

In conclusion, it appears that it is possible to account for the expansive effect of the anionic cosolutes by the present treatment, but that owing either to mobility of the bound anions or to some kind of counter-ion binding, there is a fairly constant discrepancy between the equilibrium binding constants determined by dialysis and those corresponding to the molecular size data.

Acknowledgments.—We are grateful to Dr. P. J. Flory for comments on this paper in manuscript. This work was supported in part by National Institutes of Health Contract A2253(C1).

(9) P. Molyneux, *Nature*, **202**, 368 (1964).

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A Mechanism for Tropylium Ion Formation by Electron Impact

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The formation of $C_8H_9^+$ in the mass spectrum of methylethylbenzene is found to involve loss of the β -methyl and ring methyl in the ratio 5:1, while the formation of $C_9H_{11}^+$ in the mass spectra of dimethylethylbenzenes is also found to involve loss of both the ring and β -methyls. A mechanism involving methyl loss from a substituted cycloheptatriene ion in which a selective γ -hydrogen transfer has occurred is proposed to explain these results. The mechanism is consistent with the labeling studies on the fragmentation of ethylbenzene, cycloheptatriene, and toluene, and, in addition, accounts for the small preference for loss of the methyl hydrogen in the fragmentation of toluene.

Introduction

The dissociative ionization of alkylbenzenes produces major ions of the general formula C_nH_{2n-7} . For the $C_7H_7^+$ ion ($n = 7$) extensive studies² with C^{13} and deuterium labeling have led to the conclusion that this ion, as formed from toluene,^{2a,b} ethylbenzene,^{2a} *p*-xylene,^{2c} and several other benzyl derivatives,^{2d}

does not retain the benzyl structure but has undergone ring expansion to form the symmetrical tropylium ion. The mechanism and timing of this ring expansion is not known. For toluene and xylene extensive scrambling of the ring and side-chain hydrogens occurs prior to formation of $C_7H_7^+$, suggesting that ring expansion occurs prior to the dissociation process. On the other hand, dissociative ionization of ethylbenzene to form $C_7H_7^+$ involves only loss of the β -CH₃ and it is impossible to determine whether this group is lost before, during, or after ring expansion has occurred.

The next higher homolog, $C_8H_9^+$, has also received some attention. The mass spectrum of labeled *p*-

(1) Alfred P. Sloan Research Fellow 1962–1964.

(2) (a) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); (b) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957); (c) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958); (d) H. M. Grubb and S. Meyerson, "Mass Spectra of Alkyl Benzenes," in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963.

xylylene^{2c} shows extensive scrambling of hydrogens in formation of $C_8H_9^+$ while the mass spectra of labeled ethylbenzenes³ also show extensive scrambling of the ring and α -hydrogens in formation of $C_8H_9^+$. Decomposition of $C_8H_9^+$ is known^{2d} to proceed with extensive loss of identity of both the hydrogens and carbons of the original molecule. It would appear from the labeling results and appearance potential studies, which show⁴ complete loss of positional identity in formation of $C_8H_9^+$ from *m*- and *p*-xylyl derivatives, that the $C_8H_9^+$ ion is best represented as a methyl-substituted tropylium ion.

The mass spectra of the methylethylbenzenes show a major fragmentation path involving loss of CH_3 to form $C_8H_9^+$. It appears logical to assume that this ion will also have a tropylium structure and, therefore, a study of this fragmentation process can provide valuable information on the details of the ring-expansion process. If loss of CH_3 occurs prior to ring expansion one would expect either loss of the β -methyl from the ethyl group (as found for ethylbenzene) or, alternatively, loss of both the ring and β -methyls but with different energy requirements. On the other hand, if ring expansion occurs prior to loss of CH_3 one might well expect the two methyls to become equivalent. As will be shown below an intermediate situation pertains, and the ring methyl and β -methyl are lost in the ratio 1:5 independent of electron energy. A mechanism of ring expansion is proposed which explains this result and the results obtained for the similar fragmentation process in three isomeric dimethylethylbenzenes.

Experimental

All mass spectra and appearance potentials were measured with an A. E. I. MS-2 mass spectrometer which has been described previously.⁴ Appearance potentials were determined in the usual manner⁵ using xenon to calibrate the voltage scale.

The *p*-methylethylbenzene was a commercial sample. The deuterium-labeled methylethylbenzenes and dimethylethylbenzenes were prepared by reacting the Grignard compound of the appropriate bromide with dimethyl-*d*₆ sulfate. All samples were purified by gas chromatography using a diisodecyl phthalate column.

Results and Discussion

Partial mass spectra of *p*-methylethylbenzene, *p*-methyl-*d*₃-ethylbenzene, and *p*-methylethyl- β -*d*₃-benzene are given in Table I. The spectra have been corrected for naturally occurring C¹³ and, for the labeled compounds, for 0.9% of the -*d*₂ compound as determined by low energy analysis.

TABLE I
PARTIAL MASS SPECTRA OF METHYLETHYLBENZENES

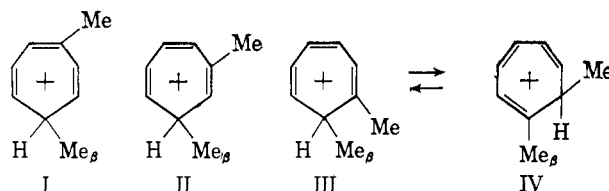
<i>m/e</i>	<i>d</i> ₀	Methyl- <i>d</i> ₃	Ethyl- β - <i>d</i> ₃
123		100.0	100.0
120	100.0		
108		257.6	56.1
107		2.5	1.0
106		7.7	4.9
105	331.4	57.4	281.5

The spectrum of the unlabeled molecule shows a peak of large intensity at *m/e* = 105 corresponding to the $C_8H_9^+$ ion formed by loss of CH_3 . In the labeled compounds part of this intensity is found at *m/e* =

105 and part at *m/e* = 108 indicating loss of both CH_3 and CD_3 . For both labeled molecules the small intensities at *m/e* = 106 and 107 are completely accounted for by further fragmentation of the *m/e* = 108 ion, indicating that the ring and β -methyls are lost without isotopic mixing. The relative intensities at *m/e* = 105 and 108 indicate that the ring methyl and the β -methyl are lost in the ratio 1:5, within experimental error. This ratio remained constant from 50-v. electron energy to the appearance potential. The appearance potentials for loss of CH_3 and CD_3 were identical, 11.2 ± 0.1 e.v., leading to $\Delta H_f(C_8H_9^+) = 226 \pm 3$ kcal./mole in agreement with values of 221–226 kcal./mole derived from appearance potential studies in the three diethylbenzenes,⁶ *m*-propylmethylbenzene,⁶ and *m*- and *p*-xylene,⁴ but much lower than the value of 252 kcal./mole found⁷ for a noncyclic $C_8H_9^+$ ion. The lower heat of formation obtained for a variety of compounds undoubtedly refers to a common cyclic structure which is best represented as a methyl-tropylium ion, although the ion is probably formed with excess energy since appearance potentials in the xylyl bromides lead⁴ to $\Delta H_f(C_8H_9^+) = 201 \pm 3$ kcal./mole.

The above results clearly indicate that loss of the ring methyl and the β -methyl yield the same fragment ions. Since the ratio for loss of the two methyls is independent of reaction conditions it would appear that the fragmentation must occur from a common intermediate; however, the two methyls have not become completely equivalent in this intermediate. We propose the following mechanism to account for these observations.

We propose that ring expansion occurs in the parent ion to form a dimethylcycloheptatriene ion by transfer of one of the α -hydrogens of the ethyl group to the attached carbon of the ring followed by insertion of the resulting $>CHCH_3$ group between any two carbons of the original benzene ring. This leads to the three intermediates I, II, and III in equal probabilities, the intermediates differing only in orientation of the two methyl groups. We further propose that loss of methyl occurs only from the 7- (or methylene) position of the three intermediates, but that in one of the intermediates a rapid intramolecular hydrogen transfer occurs between the two positions bearing a methyl group. Evidence to be presented below suggests that this transfer occurs when the two methyls are adjacent, a transfer which we shall call a 7- α -hydrogen shift. Such a shift leads to intermediate IV in equilibrium with intermediate III and to the relative abundances I:II:III:IV = 2:2:1:1. Subsequent loss of CH_3 from the methylene positions leads to five-sixths loss of the β -methyl and one-sixth loss of the ring methyl in excellent agreement with the experimental results.



(3) S. Meyerson and P. N. Rylander, *J. Am. Chem. Soc.*, **79**, 1058 (1957).
 (4) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, **84**, 4 (1962).
 (5) A. G. Harrison and T. W. Shannon, *Can. J. Chem.*, **40**, 1730 (1962).

(6) F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **22**, 1895 (1954).

(7) F. Meyer, P. Haynes, S. McLean, and A. G. Harrison, to be published.

The mass spectra of dimethylethylbenzenes show a major fragmentation path involving loss of CH_3 to form the $\text{C}_9\text{H}_{11}^+$ ion. This path is analogous to the loss of methyl from methylethylbenzene and suggests that the fragment ion may have a dimethyltropylium structure. If one applies the mechanism of ring expansion and subsequent methyl loss outlined above to the case of two methyl groups attached to the ring one reaches the conclusion that the ratio for loss of the β -methyl to the ring methyls depends on the orientation of the two ring methyls with respect to each other and on the type of hydrogen shift proposed. This is shown by the calculations summarized in Table II.

TABLE II
CALCULATED LOSS OF β -METHYL TO RING METHYL FOR
DIMETHYLETHYLBENZENES

Compound	Hydrogen shift assumed		
	7- α	7- β	7- γ
3,4-Dimethyl	2:1	2:1	13:5
3,5-Dimethyl	2:1	11:7	2:1
2,5-Dimethyl	2:1	7:2	5:4

We have, therefore, prepared and obtained mass spectra of 3,4-dimethyl-, 3,5-dimethyl-, and 2,5-dimethylethylbenzene labeled with deuterium in the β -position of the ethyl group. Partial mass spectra are given in Table III. The loss of methyl forms the

TABLE III
PARTIAL MASS SPECTRA OF DIMETHYLETHYL- β - d_3 -BENZENES
AT 50 e.v.

m/e	3,5-Dimethyl	2,5-Dimethyl	3,4-Dimethyl
137	100.0	100.0	100.0
122	56.3	54.4	81.6
119	165.8	170.0	263.3

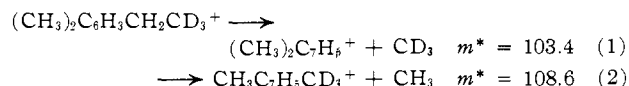
peak of greatest intensity in each spectrum and the data of Table III shows that at 50 e.v. loss of the β -methyl ($m/e = 119$) accounts for approximately 75% of the total, the remainder appearing at $m/e = 122$ and presumably involving loss of one of the ring methyls. For all three isomers the ratio 119:122 was found to vary with electron energy. Typical results are shown in Table IV for the 3,5-dimethyl isomer. For all isomers the ratio loss of $\text{CD}_3:\text{CH}_3$ remained constant at 2:1 between the appearance potential, 10.5 e.v., and approximately 12.1 e.v. Above 12.1

TABLE IV
122:119 RATIOS AS A FUNCTION OF ELECTRON ENERGY FOR
3,5-DIMETHYLETHYL- β - d_3 -BENZENE

Electron energy	Ratio, ± 0.1	Electron energy	Ratio, ± 0.1
10.9	2.0	13.5	2.3
11.1	2.0	14.5	2.4
11.3	2.0	15.5	2.5
11.5	1.9	16.5	2.6
11.7	2.1	17.5	2.7
11.9	2.0	18.5	2.8
12.1	2.0	19.5	2.9
12.3	2.1	30.0	3.1
12.5	2.2	50.0	3.1

e.v. the ratio slowly increased to 3:1. We conclude that there is one dissociation process with an appearance potential of 10.5 e.v. which, for all three isomers, involves loss of $\text{CD}_3:\text{CH}_3$ in the ratio 2:1, in addition to a direct dissociation process with an appearance potential of approximately 12.1 e.v. which involves

loss of only the β -methyl. It should be noted that the metastables for reactions 1 and 2 remained in the ratio 2:1 over the whole range of electron energies; the higher energy process apparently does not contribute to the metastable for reaction 1.



The lower energy process gives a ratio for loss of β -methyl to loss of ring methyl of 2:1 for all three isomers in agreement with the predictions of Table II assuming a 7- α -hydrogen shift following the ring expansion. Assumptions of either a 7- β - or 7- γ -shift would predict differences for the three isomers which are not found experimentally.

The mechanism of ring expansion and subsequent fragmentation proposed explains satisfactorily the labeling results involving loss of CH_3 from methyl-substituted ethylbenzenes. The two major assumptions deserve further comment. The first assumption is that ring expansion occurs by insertion of the side chain with equal probability in any position in the benzene ring. The mechanism by which this occurs is unknown but may possibly proceed through a bicyclic intermediate. Obviously extensive C^{13} -labeling will be required to provide information on the validity of this assumption. The second assumption is that the hydrogen shift occurs only between adjacent positions both bearing a methyl. Implicit in this assumption is the statement that a hydrogen shift between nonequivalent adjacent positions (*i.e.*, one bearing a CH_3 and one bearing a hydrogen) is very slow compared to the rate of hydrogen shift between equivalent positions and slow compared to the rate of loss of CH_3 . If such were not the case one would expect complete equivalence of the methyls in intermediates I to III and a 1:1 ratio for loss of the two methyls. It should be noted that the 7- α -hydrogen shift postulated for the cycloheptatriene ion in the present work differs from the 7- γ -shift observed in the thermal isomerization of cycloheptatriene⁸ and methoxycycloheptatriene.⁹ In the neutral molecule the 7- and γ -positions are close because of the boat shapes of the molecule; however, the ion may well be more planar, resembling the tropylium ion, making the 7- α -shift more probable.

It is of obvious interest to inquire whether the mechanism of ring expansion and fragmentation proposed in the present work can accommodate the isotopic-labeling results for fragmentation in other molecules leading to the tropylium ion. Recently¹⁰ it has been observed that loss of H from cycloheptatriene involves essentially complete scrambling of all hydrogens. In this case no carbon skeleton rearrangement is necessary, and a relatively small number of 7- α -hydrogen shifts in the parent ion will lead to scrambling. In this case, all positions are equivalent and it is only necessary that the rate of hydrogen shift be rapid compared to the rate of hydrogen loss.

For toluene extensive deuterium labeling^{2a,b,d,11} indicates extensive scrambling of the ring and methyl

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(10) S. Meyerson, *J. Am. Chem. Soc.*, **85**, 3340 (1963).

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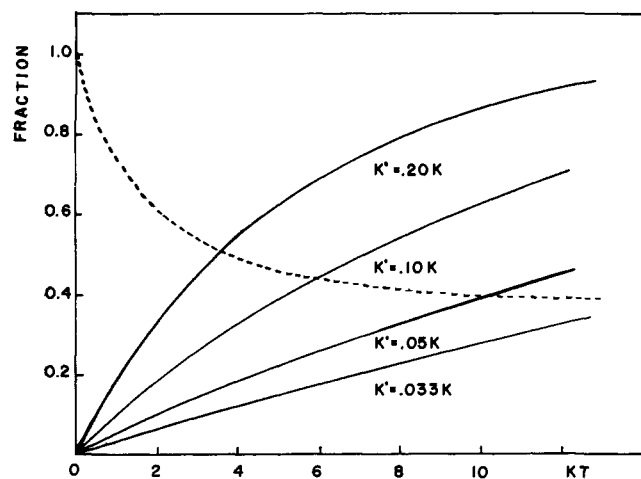
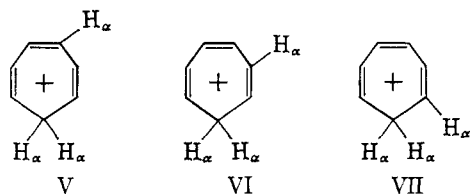


Fig. 1.—Hydrogen rearrangement and loss in toluene as a function of kt ; -----, fraction α -hydrogen in 7-position; ———, fraction total hydrogen lost.

hydrogens in formation of $C_7H_7^+$, although there is an apparent slight preference for loss of a methyl hydrogen which has been interpreted¹¹ as indicating a competitive dissociation process involving only loss of a methyl hydrogen. We suggest that the apparent preference for loss of a methyl hydrogen can be interpreted as an incomplete randomization of the hydrogens in the cycloheptatriene intermediates V, VI, and VII, rather than as a competitive direct dissociation process. The intermediates V to VII will initially have only side-chain hydrogens in the methylene positions and the fraction of side-chain hydrogens lost will depend on the rate of hydrogen loss relative to hydrogen shift.



The extensive labeling results permit an approximate calculation of these relative rates. For toluene- α - d_3 and toluene-ring- d_5 the ratios for loss of D compared to loss of H are 0.50 and 0.80, respectively.^{2d} Assuming that fragmentation occurs only from intermediates of the type shown above, these ratios reflect two effects, one an isotope effect favoring loss of H which we call i and the other a preference for loss of the α -hydrogens expressed as p .

The observed ratios for the α - d_3 and ring- d_5 compounds can be expressed as follows: α - d_3 , D:H = $3p:5i = 0.50$; ring- d_5 , D:H = $5:3pi = 0.80$. Solution of these equations gives $i = 1.58$ and $p = 1.32$. Similar results are obtained if one takes the data published for toluenes singly labeled with deuterium in ring and side-chain positions. Using $p = 1.32$, we calculate 44.2% loss of side-chain hydrogen in toluene- d_0 compared to the 37.5% expected for complete scrambling.

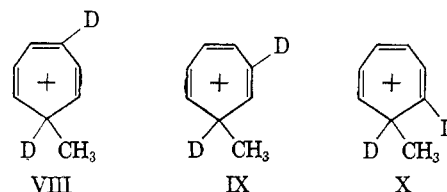
The hydrogen shifts in the intermediates V, VI, and VII can be considered as a series of consecutive unimolecular reactions all with the same rate constant, k , since all positions are equivalent. It is thus possible to calculate the fraction of side-chain hydrogen, H_α , in a methylene position as a function of the dimension-

less quantity kt . The results are shown graphically in Fig. 1. The total loss of H_α will then depend on the rate of fragmentation compared to the rate of the scrambling process. Calculations have been carried out assuming the rate of fragmentation is $1/5$, $1/10$, $1/20$, and $1/30$ the rate of hydrogen shift. Figure 1 also shows the total fraction of hydrogen lost as a function of kt for the various assumed ratios of the rate constants. The total fraction of side-chain or H_α lost can be calculated by multiplying the fraction of H_α in a methylene position in a small interval kt by the fraction of the total hydrogen loss which occurs in that interval and summing to $kt = \infty$. The percentages of side-chain hydrogen loss obtained in this fashion are given in Table V. The 44.2% estimated previously agrees with that calculated assuming a rate of hydrogen loss which is $1/20$ the rate of hydrogen shift. These relative rates do not appear unreasonable and we conclude that the labeling results in toluene can be explained by one fragmentation process in which incomplete scrambling of the hydrogen has occurred.

TABLE V
PER CENT α -HYDROGEN LOSS IN TOLUENE AS A FUNCTION OF k/k'

k/k'	5	10	20	30
% α -hydrogen loss	56.3	49.2	44.3	42.1

The labeling results for ethylbenzene show^{2a} loss of the β - CH_3 without isotopic mixing in formation of $C_7H_7^+$, and extensive scrambling of ring and α -hydrogens in formation of $C_8H_9^{+3}$. The cycloheptatriene ions formed by ring expansion can be represented as structures VIII, IX, and X for the α - d_2 case. It is apparent that the loss of CH_3 will occur without interchange of the methyl hydrogens. The scrambling in formation of $C_8H_9^+$ must indicate that hydrogen shift must occur in the ions before loss of H occurs. This necessitates a hydrogen shift between nonequivalent adjacent positions which would appear, at first, to be in conflict with earlier conclusions. However, it is only necessary to assume that the hydrogen shift is rapid compared to the rate of hydrogen loss, not with respect to the rate of loss of CH_3 . It might be noted that hydrogen loss from ethylbenzene is a minor process compared to loss of CH_3 , indicating that the rate of loss of H may be considerably slower than the rate of methyl loss.



In summary, the mechanism proposed in the present work explains in a satisfactory manner the fragmentation processes in a considerable number of benzyl and methyl-substituted benzyl derivatives. It does not appear that the mechanism can explain in a straightforward manner the labeling results for p -xylene,^{2c} nor can it be simply applied to the various other molecules which yield the $C_7H_7^+$ ion on electron impact.

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The Mechanism of Hydrogen Formation in γ -Irradiated Hydrocarbons

BY SAM Z. TOMA AND WILLIAM H. HAMILL

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The yields of cyclo-C₅H₈ and cyclo-C₅H₁₀ from radiolysis of mixtures of cyclo-C₅H₁₀ and cyclo-C₆H₁₂ are not linear in composition, unlike the yields of the corresponding cycloalkyl radicals. Additions of cyclo-C₆D₁₀ to cyclo-C₆H₁₂ decrease $G(\text{H}_2)$ and increase $G(\text{HD})$ in constant proportion. Yields of HD and D₂ from cyclo-C₆D₁₂ and cyclo-C₆D₁₀ as solutes are much less in ethanol than in alkanes. Radiolysis of 1,4-cyclo-C₆H₈ as solute in hydrocarbon solutions produces 1,3-cyclo-C₆H₈, cyclo-C₅H₇[·], and C₆H₆. All of these results are consistent with decomposition of molecular cations following electron return, loss of two hot hydrogen atoms, and formation of C=C and hot hydrogen. Alkane, alkene, and alkadiene produce alkene, diene, and triene, respectively.

Introduction

Yields of hydrogen from γ -irradiated organic liquids can be classified empirically into fractions according to the way they respond to reagents for H atoms, electrons, or positive-charge exchange.² An interesting technique which warrants further application is to add perdeuterated solute, using yields of HD and D₂ per unit solute content as evidence for mechanisms of hydrogen formation.³ Still another technique depends upon immobilizing and examining electrons, ions, and radicals in rigid media.⁴ All of these techniques have been used in a recently reported study of the mechanisms of hydrogen formation.⁵ The present report describes an extension of this work.

Experimental

Only procedures differing from those already reported⁵ will be described here.

Materials.—Phillips pure grade 3-methylpentane (3-MP) was passed through a 6-ft. column of silica gel, retaining the first one-third. Phillips research grade cyclohexane was used as received when v.p.c. boiling point columns were to be used; otherwise Fisher spectral grade cyclohexane was used. Aldrich 1,4-cyclohexadiene was used as received and stored under refrigeration. All samples were carefully outgassed in the cell by refluxing on a vacuum line.

γ -Irradiations were performed at dose rates approximating 2×10^{18} e.v./min. g. Isotopic hydrogen analyses were performed in duplicate on a CEC 21-103A mass spectrometer using a vibrating reed.

Results and Discussion

It has been proposed⁵ that an important contribution to $G(\text{H}_2)$ in cyclopentane and in cyclohexane from radiolysis at $\sim 20^\circ$ arises from the elimination of two hot H atoms when the molecular cation recombines with an electron, leaving the corresponding olefin. Each H atom is assumed to abstract hydrogen efficiently to give the corresponding alkyl radicals. It can be predicted from this mechanism that in mixtures of cyclopentane ($I = 10.53$ e.v.) and cyclohexane ($I = 9.88$ e.v.) there should be a tendency to transfer positive charge to cyclohexane (to the extent that ground-state molecular

ions are involved). Consequently, yields of cyclohexene should increase more than linearly with the concentration of cyclohexane and yields of cyclopentene should concurrently decrease to a comparable extent. The yield of free radicals from reactions of hot H atoms, on the other hand, should be linear in the concentrations of the respective hydrocarbons.

The necessary experiments have already been reported, in part, by Muccini and Schuler⁶ who have measured $G(\text{cyclo-C}_5\text{H}_9\text{I})$ and $G(\text{cyclo-C}_6\text{H}_{11}\text{I})$ at 6×10^{19} e.v./g. in liquid mixtures of these two cycloalkanes containing 0.003 *M* iodine. They found that these yields "are directly proportional to the electron fraction of the parent material present."⁶ The results from other experiments necessary to test the proposed mechanism of hydrogen formation in these mixtures appear in Table I where any departure from a proportional dependence of yield upon composition is reflected by $\Delta G = XG^0 - G_{\text{obsd}}$ (X = mole fraction and G^0 is the yield from the pure component). Yields of olefins measured without added iodine will be somewhat affected by disproportionation, but both olefins were measurable in these systems. At moderately small values of $X(\text{cyclo-C}_6\text{H}_{12})$, the yield of cyclohexene is disproportionately large and the yield of cyclopentene is correspondingly diminished. Mixtures with added iodine were also examined, corresponding to the conditions of earlier experiments,⁶ but it was not possible to measure cyclopentene reliably on the v.p.c. column because of interference by cyclopentyl iodide. The yield of cyclohexene, however, is clearly far in excess of a proportional dependence. The results of Table I in conjunction with the earlier measurements⁶ on yields of cyclopentyl and cyclohexyl radicals support the mechanism which has been proposed.

It may be suggested that these facts, the insensitivity of $G(\text{H}_2)$ to scavengers, the effect of additives to alter products from cyclohexane and cyclopentane in the ratio $\Delta G(\text{C}_6\text{H}_{11})/\Delta G(\text{C}_5\text{H}_{10}) = \Delta G(\text{C}_5\text{H}_9)/\Delta G(\text{C}_5\text{H}_8) = 2$, and the large HD/D₂ ratio in dilute solutions of perdeuterated cyclohexane in hydrocarbons, could all be accounted for by postulating ion-molecule reactions. One difficulty is that no plausible ion-molecule reaction can produce, e.g., cyclo-C₆H₁₀ + 2 cyclo-C₆H₁₁ as neutral products, while a reaction of the type

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is document COO-38-342.

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