

**Acknowledgments.**—The authors are indebted to the National Research Council of Canada and to the Alfred

P. Sloan Foundation for generous financial support of this work.

[CONTRIBUTION FROM THE RADIATION LABORATORY<sup>1</sup> AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

## The Mechanism of Hydrogen Formation in $\gamma$ -Irradiated Hydrocarbons

BY SAM Z. TOMA AND WILLIAM H. HAMILL

RECEIVED JUNE 24, 1964

The yields of cyclo-C<sub>5</sub>H<sub>8</sub> and cyclo-C<sub>5</sub>H<sub>10</sub> from radiolysis of mixtures of cyclo-C<sub>5</sub>H<sub>10</sub> and cyclo-C<sub>6</sub>H<sub>12</sub> are not linear in composition, unlike the yields of the corresponding cycloalkyl radicals. Additions of cyclo-C<sub>6</sub>D<sub>10</sub> to cyclo-C<sub>6</sub>H<sub>12</sub> decrease  $G(\text{H}_2)$  and increase  $G(\text{HD})$  in constant proportion. Yields of HD and D<sub>2</sub> from cyclo-C<sub>6</sub>D<sub>12</sub> and cyclo-C<sub>6</sub>D<sub>10</sub> as solutes are much less in ethanol than in alkanes. Radiolysis of 1,4-cyclo-C<sub>6</sub>H<sub>8</sub> as solute in hydrocarbon solutions produces 1,3-cyclo-C<sub>6</sub>H<sub>8</sub>, cyclo-C<sub>5</sub>H<sub>7</sub>·, and C<sub>5</sub>H<sub>8</sub>. 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  $\gamma$ -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.<sup>2</sup> An interesting technique which warrants further application is to add perdeuterated solute, using yields of HD and D<sub>2</sub> per unit solute content as evidence for mechanisms of hydrogen formation.<sup>3</sup> Still another technique depends upon immobilizing and examining electrons, ions, and radicals in rigid media.<sup>4</sup> All of these techniques have been used in a recently reported study of the mechanisms of hydrogen formation.<sup>5</sup> The present report describes an extension of this work.

### Experimental

Only procedures differing from those already reported<sup>5</sup> 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.

$\gamma$ -Irradiations were performed at dose rates approximating  $2 \times 10^{18}$  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 proposed<sup>5</sup> 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 Schuler<sup>6</sup> 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  $6 \times 10^{19}$  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."<sup>6</sup> 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,<sup>6</sup> 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 measurements<sup>6</sup> 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/D<sub>2</sub> 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-C<sub>6</sub>H<sub>10</sub> + 2 cyclo-C<sub>6</sub>H<sub>11</sub> 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.

(2) J. Roberts and W. H. Hamill, *J. Phys. Chem.*, **67**, 2446 (1963).

(3) W. M. Jenkinson and P. J. Dyne, *Can. J. Chem.*, **38**, 539 (1960).

(4) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963).

(5) S. Z. Toma and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1478 (1964).

(6) G. A. Muccini and R. H. Schuler, *J. Phys. Chem.*, **64**, 1436 (1960).

TABLE I  
YIELDS OF CYCLOPENTENE AND CYCLOHEXENE FROM  
MIXTURES OF CYCLOPENTANE AND CYCLOHEXANE IRRADIATED  
AT *ca.* 20° AND 10<sup>20</sup> E.V./G.

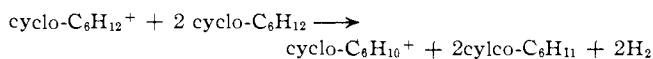
X = mole fraction C <sub>6</sub> H <sub>12</sub>	X (C <sub>5</sub> H <sub>8</sub> ) <sup>·</sup>			X (c-C <sub>6</sub> H <sub>12</sub> ) <sup>·</sup>		
	G (c-C <sub>5</sub> H <sub>8</sub> )	G <sup>0</sup> (c-C <sub>5</sub> H <sub>10</sub> ) <sup>·</sup>	ΔG	G (c-C <sub>6</sub> H <sub>10</sub> )	G <sup>0</sup> (c-C <sub>6</sub> H <sub>10</sub> )	ΔG
	No I <sub>2</sub> present					
0	2.67	2.67		0	0	
0.092	2.07	2.43	-0.36	0.47	0.22	0.25
0.229	1.73	2.06	-0.33	0.91	0.55	0.36
0.464	1.32	1.43	-0.11	1.30	1.11	0.19
1	0			2.40	2.40	
	0.01 M I <sub>2</sub> present					
0.04				0.31	0.06	0.25
0.114				0.426	0.173	0.253
0.228				0.660	0.345	0.315
0.464				1.07	0.70	0.37
0.722				1.43	1.09	0.34
0.862				1.56	1.30	0.26
1				1.51 <sup>a</sup>		

<sup>a</sup> With 0.006 M I<sub>2</sub>.<sup>5</sup>

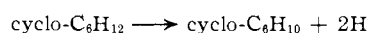
TABLE II  
HYDROGEN YIELDS FROM MIXTURES OF CYCLOHEXEDIENE-*d*<sub>10</sub> IN CYCLOHEXANE AT *ca.* 20° AND 1.3 × 10<sup>20</sup> E.V./G.

X = mole fraction c-C <sub>6</sub> D <sub>10</sub> × 10 <sup>2</sup>	G(H <sub>2</sub> )	G(HD)	G(D <sub>2</sub> )	ΔG(H <sub>2</sub> ) <sup>a</sup> /	ΔG(H <sub>2</sub> ) - 0.20/	G(HD)/	G(D <sub>2</sub> )/
				G(HD)	G(HD)	X(c-C <sub>6</sub> D <sub>10</sub> )	X(c-C <sub>6</sub> D <sub>10</sub> )
0.5	4.0	0.21	~0.007	7.1	6.2	42	~1.4
1.0	3.6 <sup>b</sup>	0.27	~0.01	7.0	6.3	27	~1.0
5.0	2.6	0.44	0.03	6.6	6.1	9	0.60
8.0	2.2	0.49	0.044	6.7	6.3	6	0.55

<sup>a</sup> Based upon G(H<sub>2</sub>) = 5.5 for cyclo-C<sub>6</sub>H<sub>12</sub>. <sup>b</sup> For the same concentration of cyclo-C<sub>6</sub>H<sub>10</sub> in cyclo-C<sub>6</sub>H<sub>12</sub>, G(H<sub>2</sub>) = 3.82 compared to G(hydrogen) = 3.88 in this run.



does not account for the fate of cyclo-C<sub>6</sub>H<sub>10</sub><sup>+</sup>, nor is it thermochemically allowed. The facts appear to require decompositions of the type



Even if the products are in their lowest energy states this reaction is about 6 e.v. endothermic and a highly excited neutral species appears to be required. Evidence has been presented that this activated entity has an ionic precursor.<sup>5</sup>

A somewhat related problem is the origin of D<sub>2</sub> from cyclohexane-*d*<sub>12</sub> in hydrocarbon solvents. Is D<sub>2</sub> entirely of molecular origin, or does it arise—at least in part—from thermalization and cage recombination of two D atoms? Parallel runs of 9 mole % cyclohexane-*d*<sub>12</sub> in 3-MP were performed at *ca.* 20 and -196° at a dose of approximately 2 × 10<sup>18</sup> e.v./g. Since reliable dosimetry was impossible for the low temperature run it is necessary to use ratios of yields. At *ca.* 20° the yields in μmoles were 7.59 H<sub>2</sub>, 0.884 HD, 0.164 D<sub>2</sub>, and 0.334 cyclo-C<sub>6</sub>D<sub>10</sub>; at -196°, 7.27 H<sub>2</sub>, 0.993 HD, 0.207 D<sub>2</sub>, and 0.304 C<sub>6</sub>D<sub>10</sub>. Since olefin is presumable the conjugate product of D<sub>2</sub> by either mechanism we compare D<sub>2</sub>/cyclo-C<sub>6</sub>D<sub>10</sub> equal to 0.49 at *ca.* 20° and 0.69 at -196°. The increased relative yield of D<sub>2</sub> at low temperature can be related to earlier work in which it was shown that considerably more geminate combination between H and I from photolyzed HI occurs at -196° than at 20° in this solvent.<sup>7</sup> Although the D-D

collision cross section is smaller than that for H-I, some enhanced yield of D<sub>2</sub> at low temperature is to be expected from the proposed mechanism which postulates formation of two hydrogen atoms from vicinal carbon atoms. The results do not exclude the possibility that an appreciable part of G(D<sub>2</sub>) may be due to a truly molecular process.

It has been shown that irradiation of cyclohexene and of cyclopentene in alkanes produce conjugated olefins, and that the processes involve ion-electron recombination.<sup>5</sup> The fate of the hydrogen was not examined then. Evidence bearing upon the question of thermal and hot hydrogen atom reactions of olefins can be obtained by examining mixtures of cyclohexene-*d*<sub>10</sub> in cyclohexane. The results in Table II suggest that D<sub>2</sub> arises in part from direct interaction of C<sub>6</sub>D<sub>10</sub> with radiation, but that HD is mainly due to a nonlinear indirect effect not involving thermal deuterium atoms. The nearly constant ratio ΔG(H<sub>2</sub>)/G(HD) indicates a predominantly substitutional effect in the radiolysis of cyclo-C<sub>6</sub>D<sub>10</sub> for cyclo-C<sub>6</sub>H<sub>12</sub>. To account for this effect we

observe that the yield of molecular hydrogen from C<sub>6</sub>H<sub>12</sub> is small on the basis of evidence from cyclo-C<sub>6</sub>D<sub>12</sub>-cyclo-C<sub>6</sub>H<sub>12</sub> mixtures.<sup>3</sup> ΔG(H<sub>2</sub>) of Table II is due in part to scavenging of thermal hydrogen atoms by cyclo-C<sub>6</sub>D<sub>10</sub>, assumed to be complete at all concentrations used and taken to be constant at G<sup>0</sup>(H); in part it is assumed to be due to charge exchange from cyclo-C<sub>6</sub>H<sub>12</sub><sup>+</sup> to cyclo-C<sub>6</sub>D<sub>10</sub> with a dependence on the yield of G<sup>0</sup>(ion) and a concentration-dependent probability of charge transfer *p*. The hot H<sub>2</sub> yield diminishes by *p*G<sup>0</sup>(ion)α, where α is the yield of hot hydrogen per ion pair for cyclo-C<sub>6</sub>H<sub>12</sub> capable of forming hydrogen. The major contribution to HD at small X(cyclo-C<sub>6</sub>D<sub>10</sub>) arises from hot deuterium reacting with C<sub>6</sub>H<sub>12</sub>, amounting to *p*·G<sup>0</sup>(ion)β, where β is the yield of hot deuterium from cyclo-C<sub>6</sub>D<sub>10</sub> per ion pair which is capable of forming hydrogen. Then

$$\frac{\Delta G(\text{H}_2)}{G(\text{HD})} = \frac{G^0(\text{H}) + pG^0(\text{ion})\alpha}{pG^0(\text{ion})\beta}$$

or

$$\frac{\Delta G(\text{H}_2) - G^0(\text{H})}{G(\text{HD})} = \frac{\alpha}{\beta} = \text{constant} \quad (1)$$

Letting G<sup>0</sup>(H) = 0.20 by trial gives the results listed in Table II. It had been estimated from other evidence that G<sup>0</sup>(H) = 0.46.<sup>5</sup> Despite the oversimplification of the mechanism, it is qualitatively clear that G<sup>0</sup>(H) must be rather small.

For comparison with the results just considered a single run with 5 mole % cyclohexene-*d*<sub>10</sub> in cyclohexene

TABLE III

ISOTOPIC YIELDS OF HYDROGEN FROM CYCLOHEXANE- $d_{12}$  AND CYCLOHEXEDIENE- $d_{10}$  UNDER VARIOUS CONDITIONS AT  $4 \times 10^{20}$  E.V./G.

Mole % solute	Solvent	$G(H_2)$	$G(HD)$	$G(D_2)$	$G(HD)/X(C_6)$	$G(D_2)/X(C_6)$
5Cyclo- $C_6D_{12}$	Cyclopentane + 0.02 MI <sub>2</sub>	3.16	0.237	0.040	4.73	0.80
5Cyclo- $C_6D_{12}$	80% Cyclopentane, 20% ethanol	4.71	0.187	0.017	3.74	0.33
2Cyclo- $C_6D_{12}$	Ethanol	4.05	0.0323	0.0023	1.64	0.12
2Cyclo- $C_6D_{10}$	Ethanol	2.70	0.0648	0.0016	3.29	0.080

TABLE IV

$\gamma$ -IRRADIATION OF 1,4-CYCLOHEXADIENE IN HYDROCARBON SOLUTIONS

Solvent	Mole %	Temp., °C.	Dose, e.v./g.	Product	G
Cyclo- $C_6H_{12}$	0.6	ca. 20	$1.2 \times 10^{19}$	1,3-Cyclo- $C_6H_8$	0.64
Cyclo- $C_6H_{12}$	0.5	ca. 20	$3.4 \times 10^{20}$	$C_6H_6$	1.2
				1,3-Cyclo- $C_6H_8$	Unidentifiable 0.2
Cyclo- $C_6D_{12}^c$	1.5	ca. 20	$1.9 \times 10^{20}$	$H_2$	0.2
				HD	0.5
				$D_2$	1.2
3-MP	0.5	-196	$1.3 \times 10^{19}$	$C_6H_6$	
3-MP	0.5	ca. 20	$1.4 \times 10^{20}$	$C_6H_6$	1.3
				1,3-Cyclo- $C_6H_8$	0.6
3-MP <sup>b</sup>	0.5	-196	$1.4 \times 10^{20}$	$C_6H_6$	0.5
				1,3-Cyclo- $C_6H_8$	0.2
3-MP <sup>c</sup>	0.5	-196	$1.4 \times 10^{20}$	$C_6H_6$	0.5
				1,3-Cyclo- $C_6H_8$	0.2

<sup>a</sup> Sample volume 0.2 cc.; product analysis semiquantitative. <sup>b</sup>  $\gamma$ -Irradiated sample thawed in dark. <sup>c</sup>  $\gamma$ -Irradiated sample optically bleached, then thawed.

was irradiated to  $1.4 \times 10^{20}$  e.v./g. to give  $G(D_2) = 2.2 \times 10^{-3}$ ,  $G(HD) = 4.0 \times 10^{-2}$ , and  $G(H_2) = 1.18$ . Again the evidence is consistent with the assumption of hot hydrogen reaction.

The results of a considerable number of experiments are consistent with the hypothesis of positive charge exchange as an important process in liquid systems under *a priori* acceptable conditions with respect to relative ionization potentials. There is evidence for an important exception to this simple rule: protonation tends to take precedence over charge exchange when both are permitted.<sup>2</sup> Ethanol protonates efficiently.<sup>8</sup>

The results in Table III show that adding ethanol to a solution of cyclohexene- $d_{12}$  in cyclopentane (in which one expects charge transfer to the solute<sup>9</sup>) diminishes both  $G(HD)$  and  $G(D_2)$ . The ratio  $G(D_2)/G(\text{cyclo-}C_6D_{10})$  is decreased from 0.44 to 0.175 for the first and second runs by adding 20% ethanol. When cyclohexene- $d_{12}$  was added to pure ethanol the values of  $G/X(C_6D_{12})$  for both HD and  $D_2$  were much smaller than had been observed in hydrocarbons with ionization potentials comparable to  $I = 10.5$  e.v. for ethanol. As an example,  $G/X$  was found to be 11.5 for HD and 2.6 for  $D_2$  in *n*-pentane ( $I = 10.55$  e.v.).<sup>9</sup> The values of  $G/X$  (cyclo- $C_6D_{10}$ ) for HD and  $D_2$  were correspondingly much less in ethanol than in cyclohexane (*cf.* Table II). There is considerable evidence that efficient formation of solute cations can occur in rigid hydrocarbon media but not in polar media (*e.g.*, amines, ethers, and alcohols). In fact, even a few per cent of polar additive markedly depresses cation yields. The evidence is consistent with charge exchange from solvent to solute, inhibited by protonating additives.<sup>10,11</sup> The results in Table III suggest the same effect, both for cyclohexane and for cyclohexene. We conclude that molecular cations are precursors of the major part of the hydrogen yield. The residual yields of HD and  $D_2$  from perdeuterated

hydrocarbons in ethanol are attributed to direct interaction with radiation.

$\gamma$ -Irradiation of cyclohexane yields monoolefin and of cyclohexene yields diolefin, and the mechanisms of hydrogen formation are similar. It is desirable to extend the observations to cyclohexadiene, choosing the 1,4-isomer as a matter of convenience. Except for one run, cyclohexane was the solvent for runs at room temperature and 3-methylpentane was used at  $-196^\circ$ . The data are summarized in Table IV.

The principal organic products were benzene, measured by v.p.c., and 1,3-cyclohexadiene, measured spectrophotometrically on the unopened sample. The extinction coefficient is  $1.0 \times 10^4$  at  $\lambda_{\text{max}}$  2600 Å. while benzene absorbs weakly in this region.<sup>12</sup> At laboratory temperature  $G(1,3-C_6H_8) = 0.64$  and  $G(C_6H_6) = 1.2$  with only *ca.* 0.5 mole % solute. An unidentifiable unsaturated product was also present with an estimated  $G \sim 0.2$ .

In a parallel run with 1,4-cyclohexadiene in cyclohexane- $d_{12}$  as solvent, there were rather large yields of  $H_2$  and HD (see Table IV) by comparison with corresponding experiments using light and heavy cyclohexane. Thus, the extrapolated yields are  $G(H_2)/X(\text{cyclo-}C_6H_8) \cong 13$  and  $G(HD)/X(\text{cyclo-}C_6H_8) \cong 33$ , suggesting that nonscavengeable hydrogen results from some energetic process such as ion recombination following charge exchange. Since  $G(H_2 + 0.5HD)$  is considerably less than  $G(\text{cyclo-}C_6H_8)$  it must be concluded that at least part of the hydrogen yield arises from thermal hydrogen atoms which are scavenged by diolefin. On the other hand,  $G(HD) \cong 0.5$  is probably not due to thermal hydrogen atoms since 1.5 mole % of diolefin should effectively remove them. We suggest that two hot hydrogen atoms are eliminated from positions 3 and 6 of cyclohexadiene, that 20% react hot giving HD, 15% thermalize and undergo geminate recombination giving  $H_2$ , while the rest diffuse away and are scavenged.

Other evidence which must be considered for runs at  $-196^\circ$  is an absorption band with maxima at 309 and

(8) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).

(9) P. J. Dyne and J. Denhartog, *Can. J. Chem.*, **40**, 1616 (1962).

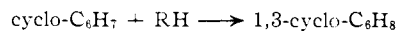
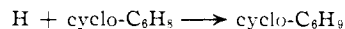
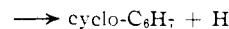
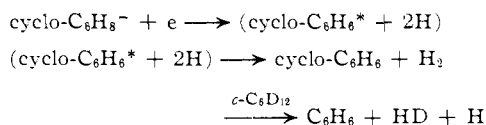
(10) J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 777 (1964).

(11) M. Kondo, M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *ibid.*, **86**, 1297 (1964).

(12) L. Pickett and E. Sheffield, *ibid.*, **68**, 217 (1946).

316 m $\mu$  which is attributed to cyclo-C<sub>6</sub>H<sub>7</sub>. This assignment rests upon the appearance of a very similar band when benzene in 3-MP was  $\gamma$ -irradiated at  $-196^\circ$ . Its formation was suppressed by addition of MTHF, a scavenger for hydrogen atoms.<sup>4</sup> The present results suggest that nascent, excited C<sub>6</sub>H<sub>6</sub> and H from 1,4-cyclohexadiene undergo cage recombination promoted by the dense glassy state. The free radical C<sub>6</sub>H<sub>7</sub> would have the lower energy 1,3-configuration and it could abstract a hydrogen from the solvent to give 1,3-cyclohexadiene. Finally, when 3-MP containing 0.5% 1,4-cyclohexadiene is  $\gamma$ -irradiated at  $-196^\circ$ , an absorption band appears at  $\lambda_{\max}$  770 m $\mu$ , quite similar to olefin cation bands observed previously,<sup>10,11</sup> together with the electron band at  $\lambda_{\max}$  1700 m $\mu$ . Optically bleaching the latter removes the cation band.

The summarized mechanism is



If this mechanism is to account for the results, it would be expected that cage effects will be more pronounced at low temperature than at room temperature. Parallel runs in 3-MP (Table IV), followed by thawing and chemical analysis, show that yields of benzene and of 1,3-cyclohexadiene are indeed much depressed at  $-196^\circ$ . This is consistent with earlier measurements of the quantum yields of hydrogen from hydrogen iodide under the same experimental conditions.<sup>7</sup>

In summary, varied evidence supports the interpretation that the major part of the hydrogen yield from radiolysis of liquid cycloalkane, -alkene, and -alkadiene arises from charge neutralization of the respective molecular cations, producing C=C and two hot hydrogen atoms.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, NEW JERSEY 07971]

## Rate and Mechanism of Proton Exchange in Aqueous Solutions of Phosphate Buffer

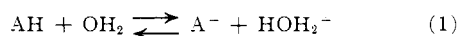
BY Z. LUZ AND S. MEIBOOM

RECEIVED JUNE 15, 1964

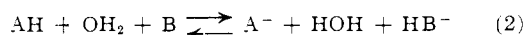
The proton transfer reaction between H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>-2</sup> in dilute aqueous solutions has been studied by n.m.r. line-broadening technique. The second-order rate constant is  $k = 1.45 \times 10^9$  mole<sup>-1</sup> l. sec.<sup>-1</sup> at 25°. It is shown that this figure is consistent with a diffusion-controlled mechanism in which the proton transfer takes place *via* two solvent water molecules.

### Introduction

The kinetics of the proton transfer between an acid and its conjugate base in solutions has been studied for a number of buffers.<sup>1</sup> In this paper we report such measurements in aqueous solutions of phosphate buffer. The n.m.r. technique used for measuring the exchange rates has been described previously.<sup>2,3</sup> In the present case the rate of proton exchange between the various phosphate ions and water is very high, and only a single sharp proton line, resulting from the averaged-out proton lines of the phosphate buffer and solvent water, is observed. It is, however, possible to measure this rate indirectly, by measuring its contribution to the rate of proton exchange between solvent water molecules. The latter rate can be measured by using <sup>17</sup>O-enriched water. References 2 and 3 present a detailed description of the method used. Only those reactions in which the solvent water participates in the exchange process can be measured by this method. Simple examples of such mechanisms are of the type



or



where AH symbolizes an acid and B a base. AH and B are not necessarily neutral molecules and the charges in eq. 1 and 2 are meant to indicate differences only. Reactions of type 2, in which the proton transfer takes place through one or more water molecules (which may be thought of as belonging to the solvation shells of the buffer components) have been found to be important in many systems.<sup>1</sup>

In reactions 1 and 2 the buffer can be looked upon as catalyzing the proton exchange between water molecules. The rate of the latter process is obtained from the broadening of the proton peak in <sup>17</sup>O-enriched water. In principle very high rate constants for reactions 1 and 2 can be measured, since the rate of proton exchange in water can be kept within measurable limits by using sufficiently low buffer concentrations.<sup>3</sup>

### Results

A number of solutions of constant buffer ratio [NaH<sub>2</sub>PO<sub>4</sub>]/[Na<sub>2</sub>HPO<sub>4</sub>] = 1.70 and Na<sub>2</sub>HPO<sub>4</sub> concentrations between about 0.008 and 0.03 M were made up. The solvent water was enriched to 0.33 atom % <sup>17</sup>O. The proton relaxation times  $T_1$  and  $T_2$  of these solutions were measured by the spin-echo technique as described before.<sup>2,3</sup> From these quantities the average lifetime between successive transfers of a proton in water,  $1/\tau$ , is calculated using eq. 3 of ref. 3. The result is plotted in Fig. 1 as a function of the square of the buffer concentration. All measurements relate to a temperature of

(1) For a review and references see the articles of H. Strehlow and of M. Eigen and L. De Maeyer, in "Technique of Organic Chemistry," Vol. VIII, Arnold Weissberger, Ed., 2nd Ed., Part II, Interscience Publishers, Inc., New York, N. Y., 1963.

(2) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **39**, 366 (1963).

(3) Z. Luz and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 3923 (1963).