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Kinetics of Ionic Processes in the Radiolysis of Liquid Cyclohexane<sup>1</sup>

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Ammonia-*d*<sub>3</sub> has been used as a proton scavenger in the radiolysis of liquid cyclohexane. The kinetics of proton transfer from cyclohexane ions have been studied by measuring the yield of HD as a function of ND<sub>3</sub> concentration. In agreement with other work, the *G*-yield of free ions is 0.08. The majority of ions undergo geminate recombination, but it is estimated that the lifetimes of about half these ions lie in the range 10<sup>-9</sup> to 10<sup>-7</sup> sec. Ionic reactions can therefore proceed in the presence of high concentrations of a very reactive scavenger. A simple diffusion model of geminate ionic recombination predicts a lifetime for the ion pair which varies as the cube of the initial separation distance. Calculations according to this model are in semiquantitative agreement with the experimental results.

## Introduction

Previous work has demonstrated that ionic intermediates are responsible for the radiation-induced polymerization of isobutylene,<sup>2,3</sup>  $\alpha$ -methylstyrene,<sup>4</sup> and cyclopentadiene.<sup>5</sup> From a study of the latter system,<sup>5</sup> it has been deduced that while the individual ion lifetime during propagation is of the order of 10<sup>-3</sup> sec., the yield of ionic initiators is rather low, and corresponds to a 100-e.v. yield (*G*-value) of about 0.2. Recently, conductivity and mobility measurements on radiolytic ions in saturated hydrocarbons<sup>6,7</sup> have provided two determinations of the *G*-yield of free ions,<sup>8</sup> *viz.*, 0.09  $\pm$  0.04 (Allen and Hummel<sup>6</sup>) and *ca.* 0.2 (Freeman<sup>7</sup>). The similarity between the *G*-values for the initiation of ionic polymerization and for free ions suggests a common identity, and this proposition is supported by calculations on the lifetime of these ions.<sup>9</sup>

The clear implication of the low *G*-value for free ions in liquid hydrocarbons is that most ions (*G ca.* 3) undergo fast geminate recombination,<sup>6</sup> but the important question remains as to the time scale of this process. Even if the mean lifetime,  $\tau$ , of an ion with respect to geminate recombination is much less than 10<sup>-3</sup> sec., the ion will react with a scavenger molecule present in a concentration [S] with a probability exceeding 0.5 provided  $\tau \geq 1/k_s[S]$ , where  $k_s$  is the rate constant for the ion-molecule reaction. Thus, information bearing on the kinetics of geminate ionic recombination can be obtained by the use of a very reactive scavenger,<sup>10</sup> and this paper reports a study along these lines.

The choice of a suitable system was influenced by several considerations. Since our previous experience had already indicated the potency of ammonia as a retarder of radiation-induced ionic polymerization,<sup>5,11</sup> and because proton transfer reactions are often charac-

terized by rate constants in excess of 10<sup>9</sup> M<sup>-1</sup> sec.<sup>-1</sup>,<sup>12</sup> an investigation of exothermic proton transfer from cyclohexane ions to ND<sub>3</sub> appeared to be feasible, especially in view of the fact that ion-molecule reactions of this type are known to occur for hydrocarbon ions in the mass spectrometer.<sup>13</sup> Neglecting any isotope effect, the neutralization of ND<sub>3</sub>H<sup>+</sup> product ions is assumed to give D atoms with a statistical probability of 3:4, followed by hydrogen atom abstraction from the cyclohexane solvent to form HD. Accordingly, the extent of proton transfer can be evaluated from the fraction of HD in the hydrogen gas produced during radiolysis. Preliminary results<sup>5</sup> on this system showed that the order of magnitude of HD formation could not be accounted for in the absence of reactivity transfer from cyclohexane to ammonia. The possibility that significant amounts of HD could arise by some means other than proton transfer seems remote; ammonia is relatively unreactive to hydrogen atoms<sup>14</sup> and apparently does not attach electrons in a saturated hydrocarbon glass,<sup>16</sup> while positive charge transfer from cyclohexane to ammonia would be endothermic.<sup>5</sup>

## Experimental

Eastman Spectrograde cyclohexane was passed through a column of activated silica gel and degassed on a vacuum line. Subsequently, the cyclohexane was distilled twice *in vacuo* onto fresh sodium mirrors; after the liquid had been left in contact with the sodium surfaces for periods of hours, a sample was finally distilled into a cylindrical Pyrex glass ampoule of about 30-ml. capacity. These ampoules were fitted with a diaphragm break-seal at the closed end and the join to the vacuum line was suitably constricted. Ammonia-*d*<sub>3</sub> (Merck Sharp and Dohme of Canada Ltd.) was freed from traces of air and moisture by pumping on the condensed solid after trap-to-trap distillation onto sodium metal surfaces. For each experiment, a prescribed volume of ammonia-*d*<sub>3</sub> was measured in a calibrated Toepfer pump under standard conditions and then admitted into an ampoule containing frozen cyclohexane at -196°. The sample was sealed off at the con-

(1) This research is supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968.

(2) W. H. T. Davison, S. H. Pinner, and R. Worrall, *Proc. Roy. Soc. (London)*, **A252**, 187 (1959).

(3) E. Collinson, F. S. Dainton, and H. A. Gillis, *J. Phys. Chem.*, **63**, 909 (1959).

(4) J. V. F. Best, T. H. Bates, and F. Williams, *Trans. Faraday Soc.*, **58**, 192 (1962).

(5) W. R. Busler, D. H. Martin, and F. Williams, *Discussions Faraday Soc.*, **36**, 102 (1963).

(6) A. O. Allen and A. Hummel, *ibid.*, **36**, 95 (1963).

(7) G. R. Freeman, *J. Chem. Phys.*, **39**, 988 (1963).

(8) The term *free ions* is used to denote ions that undergo random recombination with oppositely charged species by homogeneous second-order kinetics.

(9) F. Williams, *Discussions Faraday Soc.*, **36**, 254 (1963).

(10) The theory of scavenger competition with the geminate recombination of free-radical pairs has been discussed by R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).

(11) M. A. Bonin, W. R. Busler, and F. Williams, *ibid.*, **84**, 4355 (1962).

(12) Cf. M. Eigen, *Angew. Chem. Intern. Ed.*, **3**, 1 (1964). In the present case, an upper limit for  $k_s$  is set by the Debye expression [P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942)].  $k_s = \gamma 8RT/3000\eta$ , where  $\gamma$  represents the correction factor for ion-ammonia dipole interaction,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $\eta$  is the viscosity. At  $T = 300^\circ\text{K}$ ,  $\gamma \sim 2$ ,  $\eta(\text{cyclohexane}) = 9 \times 10^{-2}$  poise, hence  $k_s = 1.5 \times 10^{10} \text{ M}^{-1} \text{ sec.}^{-1}$ .

(13) V. L. Tal'rose and E. L. Frankevich, *Proceedings of the First All-Union Conference on Radiation Chemistry*, Academy of Sciences, Moscow, U.S.S.R., 1957, part 1, p. 11.

(14) M. Schiavello and G. G. Volpi, *J. Chem. Phys.*, **37**, 1510 (1962). These authors estimate that the rate constant for the reaction,  $\text{H} + \text{NH}_3 \rightarrow \text{H}_2 + \text{NH}_2^+$ , does not exceed *ca.* 10<sup>3</sup> M<sup>-1</sup> sec.<sup>-1</sup> at 150° in the gas phase. Adopting their lower estimate of 10 kcal./mole for the activation energy, the rate constant for this reaction would be of the order of 10<sup>2</sup> M<sup>-1</sup> sec.<sup>-1</sup> at 25°. This value is considerably less than the rate constant<sup>15</sup> of 6.6  $\times 10^6$  M<sup>-1</sup> sec.<sup>-1</sup> for the corresponding abstraction process from cyclohexane at 23°.

(15) T. J. Hardwick, *J. Phys. Chem.*, **65**, 101 (1961).

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

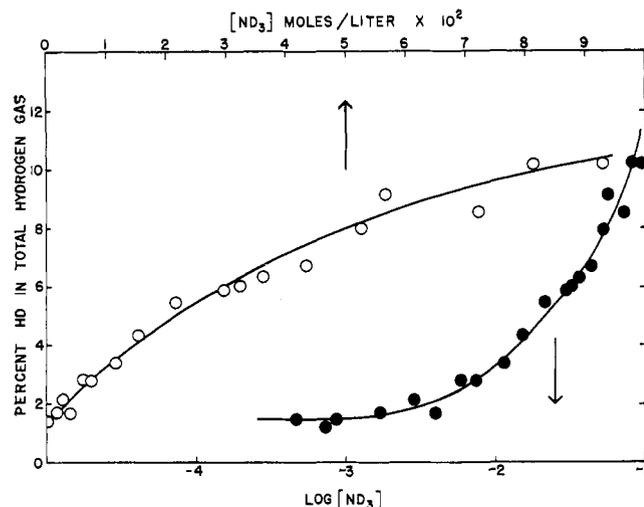


Fig. 1.—Per cent HD yield in total hydrogen gas as a function of  $\text{ND}_3$  concentration (open circles) and  $\log [\text{ND}_3]$  (solid circles).

striction which protruded just above the surface of the liquid nitrogen coolant. All the experiments reported in this paper refer to about 20 g. of cyclohexane per ampoule and a vapor phase volume (at 25°) not in excess of 5 ml. Concentrations of ammonia- $d_3$  in the cyclohexane are calculated on the basis of complete gas solubility.

All irradiations were carried out in cobalt-60  $\gamma$ -sources at ambient room temperature. Dose rates were determined by the Fricke dosimeter and the values (in e.v.  $\text{g}^{-1} \text{min}^{-1}$ ) multiplied by the ratio (1.030) of electrons per gram in cyclohexane to 0.8  $\text{N H}_2\text{SO}_4$ .

After irradiation, the volatile gas at  $-196^\circ$  was transferred and measured through a calibrated Toepler pump into a storage bulb. The gross composition and the isotopic distribution of molecular hydrogen in the gas samples were determined using a mass spectrometer.

## Results

It is well known that the  $G$ -yield of hydrogen from the radiolysis of pure cyclohexane decreases as the dose is increased. It follows that in order to evaluate the effect of  $\text{ND}_3$  concentration on the total hydrogen yield, the results should refer to the same total dose. The data given in Table I correspond to this require-

TABLE I  
 $G$ -YIELDS AND ISOTOPIC CONTENT OF HYDROGEN GAS FROM THE RADIOLYSIS OF CYCLOHEXANE- $\text{ND}_3$  SOLUTIONS

Expt.	$[\text{ND}_3]$ , mole/l.	Dose $\times 10^{-19}$ e.v./g.	$G$ , 100 e.v.	—Isotopic composition—		
				$\text{H}_2$	HD	$\text{D}_2$
E34	$8.8 \times 10^{-4}$	4.11	5.29	98.57	1.43	..
E38	$2.97 \times 10^{-3}$	4.08	5.37	97.88	2.12	..
E39	$5.96 \times 10^{-3}$	4.08	5.08	97.21	2.78	0.01
E33	$1.53 \times 10^{-2}$	4.11	5.19	95.69	4.30	0.01
E37	$2.95 \times 10^{-2}$	4.08	5.00	94.15	5.84	0.01
E32	$3.61 \times 10^{-2}$	4.11	5.07	93.68	6.29	0.03
E36	$7.2 \times 10^{-2}$	4.08	4.91	91.43	8.53	0.04

ment and show that there is only a very slight decrease of about 0.3 in the  $G$ -value over the range of ammonia concentration used. For the dilute solutions, the  $G$ -yield of 5.3, within error limits of 0.1, is in close agreement with another value<sup>17</sup> obtained for pure cyclohexane at the same total dose. Some of our preliminary data<sup>5</sup> indicated slightly higher  $G$ -values than those reported here, and there are other literature values<sup>18</sup> for

(17) P. J. Dyne and J. A. Stone, *Can. J. Chem.*, **39**, 2381 (1961).

(18) L. J. Forrestal and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 1535 (1961).

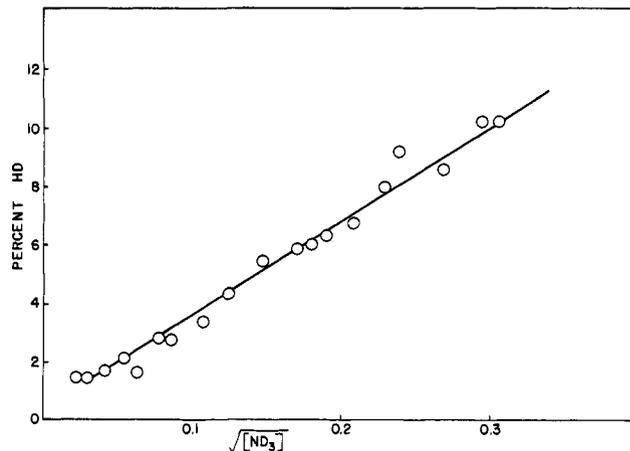


Fig. 2.—Dependence of per cent HD yield on the square root of the  $\text{ND}_3$  concentration  $[\text{ND}_3]$  in moles/l.

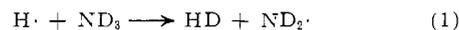
$G(\text{H}_2)$  from cyclohexane extending up to 5.8 at very low total doses.

For duplicate runs in which the ammonia content was similar, a variation of the vapor space in the ampoule within the range 0.5 to 5 ml. caused no significant variation in the HD yields. Thus it seems reasonable to assume that most of the  $\text{ND}_3$  was present in the liquid phase under these conditions. The majority of the results were obtained with a vapor space of approximately 2 ml. and a liquid volume of 25 ml.

In Fig. 1, the per cent yields of HD are plotted against linear and logarithmic functions of the  $\text{ND}_3$  concentration. A feature of these plots is the limiting yield of about 1.5% HD at concentrations of scavenger below *ca.*  $10^{-2} M$  down to  $4 \times 10^{-4} M$ . At higher concentrations of  $\text{ND}_3$  up to  $10^{-1} M$ , the yield of HD rises to over 10%; over this latter concentration range, a plot of the log HD yield against  $\log [\text{ND}_3]$  gave a linear relation with a slope of 0.52. Since this result indicated a dependence of the HD yield on the square root of the  $\text{ND}_3$  concentration, a test of this relation is reproduced in Fig. 2.

## Discussion

Before discussing the results in relation to the postulated proton-transfer mechanism, it is worthwhile to use the data to reinforce the previous arguments against the contribution of other recognizable processes to the HD yield. In the first place, the direct effect on  $\text{ND}_3$  may be considered as a source of D atoms. The initial slope of the yield-concentration curve in Fig. 1 corresponds to a HD yield of 9.4  $G$ -units per unit of molar concentration of  $\text{ND}_3$  or to a  $g(\text{HD})$  value<sup>19</sup> of 87 per unit mole fraction of  $\text{ND}_3$ . Accepting the electron fraction as a basis for the partition of energy between the two components, the above result would entail a primary yield of D atoms from  $\text{ND}_3$  corresponding to a  $G(\text{D}\cdot)$  of 417. Of course, such a high value is completely unrealistic, and it is pertinent to recall that a  $G(\text{H}\cdot)$  value of 1.75 has been determined for the radiolysis of liquid ammonia.<sup>20</sup> Secondly, to account for the above value of  $g(\text{HD})$  by the reaction



(19) This notation is the same as that used by P. J. Dyne and W. M. Jenkinson, *Can. J. Chem.*, **39**, 2163 (1961), where  $g(\text{HD})$  is defined as  $\partial G(\text{HD})/\partial X_{\text{D}}$  at low mole fractions  $X_{\text{D}}$  of the deuterium compound.

(20) D. Cleaver, E. Collinson, and F. S. Dainton, *Trans. Faraday Soc.*, **56**, 1640 (1960).

would require that the rate constant  $k_1$  exceed the rate constant  $k_2$  for the corresponding abstraction from cyclohexane by a factor of 20. Since the published



values<sup>14,15</sup> suggest that the ratio  $k_1:k_2$  is of the order of  $10^{-5}$  at 25°, and in view of the conclusion<sup>20</sup> that H atoms combine with one another rather than abstract in liquid ammonia, it can be safely concluded that the present results are incompatible with a mechanism based on reaction 1.

It is also of some interest to compare the  $g(\text{HD})$  value obtained in this work with some corresponding results for hydrocarbon mixtures.<sup>19,21</sup> The value of  $g(\text{HD})$  from cyclohexane-cyclohexane- $d_{12}$  mixtures is between 3.6 and 4.1<sup>19,21</sup>; higher values of  $g(\text{HD})$  ranging up to 11.5 have been obtained for solutions of cyclohexane- $d_{12}$  in the lower paraffins. These positive changes in  $g(\text{HD})$  have been attributed<sup>21</sup> to interactions involving excited or charged intermediates such that the deuterated molecule (cyclohexane- $d_{12}$ ) displays an enhanced reactivity in such solvents. With solutions of  $\text{C}_6\text{H}_{12}$  in hydrocarbons of higher molecular weight, converse effects have been reported.<sup>21</sup> Insofar as the deviation of  $g(\text{HD})$  from a value of about 4 is a measure of reactivity transfer from an activated hydrocarbon molecule to a deuterated acceptor, it can be concluded that the "transfer efficiency" to  $\text{ND}_3$  is an order of magnitude greater than for a favorable transfer to another hydrocarbon molecule. This reactivity transfer between different hydrocarbon molecules can be correlated with a lower ionization potential for the acceptor.<sup>21</sup> On the other hand, charge transfer cannot occur from cyclohexane ions to  $\text{ND}_3$ , at least not unless excited ions are responsible.

Arguments that merely demonstrate the implausible nature of other mechanisms offer insufficient grounds for the adoption of yet another, less objectionable, mechanism. Since the main function of mechanistic formulations lies in the promotion of useful correlations between independent systems, a reliable mechanism must satisfy the stringent test of general consistency. It is now appropriate to scrutinize the proton-transfer mechanism from this vantage point.

The limiting yield of HD at low concentration of scavenger is plainly indicative of a steady-state reaction in which the scavenger concentration is not a determining factor above a certain minimum value necessary for complete scavenging.<sup>10,22</sup> On the basis of the proton-transfer mechanism, the 1.5% HD yield corresponds to  $G(\text{ions}) = 0.08$ , uncorrected for any statistical loss of H atoms from the product ion. In this instance, the mean lifetime of the steady-state ions (*ca.*  $10^{-2}$  sec.) would permit many encounters of  $\text{ND}_3\text{H}^+$  ions and  $\text{ND}_3$  molecules with ensuing exchange. The  $G$ -value of 0.08 for steady-state ions is in general agreement with the previous results obtained for saturated hydrocarbons by physical methods<sup>6,7</sup>; moreover, similar yields have been reported<sup>23</sup> for mixtures of cyclohexane

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

(22) A rough order of magnitude estimate of the scavenger concentration  $[S]$  which would capture 99% of the free ions in the steady state can be made as follows. We take  $k_3 = 10^7 M^{-1} \text{sec}^{-1}$ ,  $k_1$  (recombination rate constant for ions) =  $10^{12} M^{-1} \text{sec}^{-1}$  (calculated from ref. 6), and  $G(\text{free ions}) = 0.1$ . At the appropriate dose rate of  $10^{13}$  e.v.  $l^{-1} \text{sec}^{-1}$ , it follows that the steady-state concentration of ions  $[I]$  is  $1.3 \times 10^{-10} M$ , so  $k_3[S_{\text{min}}] = 10^4 k_1[I] = 10^4 \text{sec}^{-1}$ . Hence  $[S] \geq 10^{-5} M$ , or  $\log [S] \geq -5 \pm 1$ .

(23) W. Van Dusen, *Discussions Faraday Soc.*, **36**, 260 (1963).

and  $\text{D}_2\text{O}$ . Also, it can be concluded that the demonstration of free-ion scavenging by low concentrations of ammonia in cyclohexane provides emphatic support for the interpretation of ammonia retardation in radiation-induced cationic polymerization.<sup>5</sup>

Turning to the dependence of the HD yield at higher scavenger concentration ( $>10^{-2} M$ ), this region obviously corresponds (compare ref. 10) to the situation where ammonia is competing with the geminate recombination of ions. It is remarkable that the yield increases as the square root of the  $\text{ND}_3$  concentration, since this result parallels the predictions<sup>10,24</sup> for scavenger competition with the geminate recombination of free radicals. For reasons given below, it is felt that this parallelism is merely accidental and without theoretical significance. First of all, a pair of ions will not undergo random diffusive displacements relative to one another because of the superimposition of their mutual Coulombic attraction on the Brownian movement. Secondly, the lifetime of an ion undergoing geminate recombination would be expected to be a rather sensitive function of initial separation distance (*vide infra*), and therefore the kinetics would in turn depend on the detailed statistics of separation. Lastly, the situation is further complicated by our complete ignorance of the nature of the negative species.

In the model suggested by Samuel and Magee,<sup>25</sup> the ejected electron was considered to be thermalized and recaptured by the parent ion in a time of about  $10^{-13}$  sec. However, there are many uncertainties about this calculation, especially in regard to the mechanism of energy loss sustained by the electron.<sup>26,27</sup> In this connection, the transient formation of negative ion states has been considered as a contributory factor.<sup>26</sup> It is also relevant to recall the experiments of LeBlanc<sup>28</sup> on electron-drift mobility in liquid *n*-hexane. This latter work indicates that electrons can migrate between low energy traps such that the electrons behave neither as free entities nor as true molecular anions. Now, in considering the time scale for geminate recombination, the nature of the negative entity is of obvious significance, and this is especially true regarding the details of the return journey after thermal equilibrium has been attained.

Although the problem defies a rigorous theoretical approach, some headway can be made by considering the electron to be trapped as some kind of negative entity with molecular dimensions. The situation now corresponds to the diffusion of ions of opposite charge under the influence of their mutual Coulombic force field. Application of the Nernst-Einstein relation leads to the equation

$$\frac{\partial r / \partial t}{-\partial E(r) / \partial r} = \frac{D}{kT} \quad (3)$$

where  $\partial r / \partial t$  is the relative velocity at a separation distance  $r$ ,  $-\partial E(r) / \partial r$  is the Coulombic force =  $-e^2 / \epsilon r^2$ ,  $e$  is the absolute charge on each ion,  $\epsilon$  is the dielectric

(24) J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *J. Am. Chem. Soc.*, **76**, 3274 (1954).

(25) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1085 (1953).

(26) J. L. Magee, *Discussions Faraday Soc.*, **36**, 247 (1963).

(27) M. Magat, *ibid.*, **36**, 256 (1963).

(28) O. H. LeBlanc, Jr., *J. Chem. Phys.*, **30**, 1443 (1959). LeBlanc obtained a value of  $1.4 \times 10^{-3} \text{cm}^2/\text{v} \cdot \text{sec}$ . for electron drift mobility in liquid *n*-hexane, which corresponds to a diffusion coefficient of  $3.5 \times 10^{-6} \text{cm}^2 \text{sec}^{-1}$  at 300°K.

constant of the medium,  $D$  is the sum of the ionic diffusion coefficients in the medium,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. Rearrangement and integration leads to eq. 4 for the time  $\tau$  of recombination from an initial separation distance  $r$ .

$$\tau = -\frac{kT\epsilon}{De^2} \int_r^0 r^2 dr = \frac{kT\epsilon}{3De^2} r^3 \quad (4)$$

It is now of interest to calculate  $\tau_c$  for the separation distance  $r_c$ , defined by  $-E(r_c) = e^2/\epsilon r_c = kT$ , where the mutual Coulombic potential energy  $E(r_c)$  balances the energy of Brownian motion. To a first approximation,  $\tau_c$  can be identified as the maximum lifetime of a pair of ions undergoing geminate recombination. For cyclohexane as the medium,  $\epsilon = 2.0$  and  $D \simeq 2.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ .<sup>7</sup> The appropriate calculation reduces to  $\tau_c = r_c^2/3D = 1.1 \times 10^{-7} \text{ sec.}$  for recombination from  $r_c = 280 \text{ \AA.}$  at  $300^\circ\text{K.}$  Since  $\tau$  is proportional to  $r^3$ , a recombination time of  $10^{-9} \text{ sec.}$  corresponds to  $r = 60 \text{ \AA.}$  Although this treatment based on the Nernst-Einstein relation may not be valid at very short separation distances<sup>29</sup> owing to the large forces of attraction which will then apply, it should serve as a useful approximation for  $r$ -values of the order of  $100 \text{ \AA.}$  which are of primary interest to the ensuing discussion.

Returning to the experimental findings, the onset of scavenger competition with geminate recombination occurs between  $10^{-3}$  and  $10^{-2} M$   $\text{ND}_3$  concentration (Fig. 1); this result corresponds to the scavenging of ions with a mean lifetime,  $\tau$ , in excess of  $1/k_s[10^{-2}]$  or  $10^{-7} \text{ sec.}$  where  $k_s$  is taken as before to be  $10^9 M^{-1} \text{ sec}^{-1}$ . Thus, the experimental result is in semi-quantitative accord with the previous theoretical calculation of  $\tau_c$ . Although such agreement does not prove that the suggested model is correct, it is difficult to conceive of a model based on a free electron which would allow times of this magnitude ( $10^{-7} \text{ sec.}$ ) to elapse before geminate recombination. If the proposed model is valid, then the results at  $10^{-1} M$  (after statistical correction) can be taken to indicate that at least 14% of the total ions achieve separation distances greater than  $130 \text{ \AA.}$  Whether all the ions can be "captured" at high scavenger concentration is a matter of conjecture; this will obviously depend on the radial distribution function  $P(r)$  for initial separation distances. Extrapolation of the empirical dependence of yield on the half-power of scavenger concentration suggests that molar concentrations of a very reactive scavenger would re-

(29) The mean displacement (drift),  $\Delta r$ , of an univalent ion (mass  $M$ ) in the direction of the force during the relaxation time ( $t = \lambda/(8kT/\pi M)^{1/2} \simeq 10^{-12} \text{ sec.}$  for mean free path  $\lambda$  of  $3 \text{ \AA.}$ ) between molecular encounters is given by  $\Delta r = 1/2[-(\partial E/\partial r)/M]t^2$ . At  $r = 100 \text{ \AA.}$ ,  $\Delta r$  is  $0.040 \text{ \AA.}$ , and the increment of energy  $\Delta E$  acquired under the influence of the Coulombic force is  $2.9 \times 10^{-5} \text{ e.v.}$  Hence  $\Delta E/kT$  is of the order of  $10^{-3}$  at room temperature, and the excess energy is easily dissipated by subsequent repeated collisions within the solvent cage before the next jump. Deviations from the Nernst-Einstein relation might only be expected to occur when  $\Delta E \geq kT$ ; in the present case this condition corresponds to  $r \leq 19 \text{ \AA.}$

act with about 50% of the ions. If this is the case, then the above model implies that the value of  $r_m$  corresponding to  $\int_0^{r_m} P(r)4\pi r^2 dr = 0.5$  is  $\sim 60 \text{ \AA.}$  This value may be compared with Onsager's estimate<sup>30</sup> that the median diffusion range of electrons before attachment to oxygen molecules in air at 100 atm. pressure is of the order of  $500 \text{ \AA.}$  The ratio of these two values approximates to the reciprocal of the relative densities in the two systems, so  $r_m \approx 60 \text{ \AA.}$  can therefore be considered reasonable.

There is a tendency to assume that the free-ion yield is due entirely to ions which have achieved an initial separation distance greater than  $r_c$ . That is to say, the fraction  $f$  of free ions is given by

$$f = \int_{r_c}^{\infty} P(r)4\pi r^2 dr$$

Strictly speaking, for all cases of molecular diffusion, this is incorrect and should be replaced<sup>30</sup> by the function

$$f = \int_0^{\infty} P(r)4\pi r^2 \exp(-e^2/\epsilon r kT) dr$$

since there is always a finite probability of escape  $\exp(-e^2/\epsilon r kT)$  at any distance  $r$ . It seems worthwhile to point this out anew because it could vitiate estimates of  $f$  based only on counting  $\delta$ -rays exceeding a certain energy.

Nothing has been said concerning the nature of the transient positive ion in cyclohexane. The only assumption which has been made is that the species in question is a Brønsted acid<sup>9</sup> which could be either the parent ion  $\text{C}_6\text{H}_{12}^+$  or protonated cyclohexane  $\text{C}_6\text{H}_{13}^+$ , depending upon the relative proton affinities of the cyclohexyl radical and cyclohexane molecule. No loss of generality is involved in this ambiguity. Recent theoretical considerations<sup>31</sup> on  $\text{H}_3^+$  appear to concur with the view that such species are perhaps best described in terms of a proton located in the charge cloud of the residual free radical or molecule.

The conclusions of this work may now be summarized. A free-ion yield,  $G = 0.08$ , has been measured for liquid cyclohexane. Most ions do not escape their oppositely charged partners but undergo geminate recombination with times less than  $10^{-7} \text{ sec.}$  and a probable median time of  $10^{-9} \text{ sec.}$  This time scale permits ionic reactions to proceed at high concentrations ( $>10^{-2} M$ ) of a very reactive scavenger.

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(30) L. Onsager, *Phys. Rev.*, **54**, 554 (1938).

(31) H. Shull, *J. Am. Chem. Soc.*, **86**, 1469 (1964).