then washed with liquid ammonia several times. After the final washing, the system was pumped down to a pressure of 10^{-2} mm. and one atmosphere of argon was admitted. The tube was quickly transferred to an argon-filled dry box and the product was transferred to small screw-cap bottles (1.0 g. yield).

Analysis of $Et_4NN(C_6H_5)_2$.—Samples were weighed out in the argon dry box into erlenmeyer flasks and, after removing from the dry box, about 50 ml. of water was added (while the samples were under a blanket of argon). The material immediately hydrolyzed and left a suspension of white diphenylamine. The solutions were titrated with 0.1 *N* hydrochloric acid to determine the amount of tetraethylammonium hydroxide, and the precipitate of diphenylamine was filtered off and weighed. Typical analysis: Et_4N^+ calcd., 43.6%; found, 41.2, 40.1%. $N(C_6H_5)_2^-$ calcd., 56.4%; found, 57.4, 59.9%. The above method of analysis does not completely distinguish between $Et_4NN(C_6H_5)_2$ and $NaN(C_6H_5)_2$, since both materials hydrolyze to give a suspension of diphenylamine in a basic solution. So two separate samples were analyzed for sodium by igniting to dryness with sulfuric acid and were found to contain only 0.08 and 0.1% sodium. Another sample (containing about 15% diphenylamine impurity) was analyzed for Et_4N^+ by running a Kjeldahl analysis on the aqueous solution remaining after hydrolysis and titration. Et_4N^+ calcd., 43.6%; found by Kjeldahl, 34.3%; found by titration, 37.3%. No preparation ever analyzed better than 94% pure, diphenylamine being the usual impurity.

Stability of $Et_4NN(C_6H_5)_2$.—When $Et_4NN(C_6H_5)_2$ is gradually heated in an evacuated closed system, decomposition (as evidenced by gas evolution) starts at 75–80°. At 100°, decomposition is very rapid and the material melts and effervesces. The gas evolved from one sample was analyzed mass spectrometrically (98% ethylene was found); the amount of gas evolved was approximately 100% of theory (accounting for the impurities present).

When the material is held over a flame, it quickly ignites, leaving a gummy residue which is slightly more difficult to ignite. Dry air causes the material to turn dark green in one day, and after one week, a dark viscous liquid remains. This residue dissolves in organic solvents to give colored solutions, the color apparently depending on the time of exposure to air. Because of this reactivity to air, it is necessary to store $Et_4NN(C_6H_5)_2$ in sealed glass vials or tight-fitting screw-cap bottles.

Acknowledgments.—The author is grateful to Dr. Donald R. Bomberger and Mr. Antoine A. Franke for many of the chemical analyses. Mr. Herbert X. Di Grazia and Mrs. Bobby Mohler carried out the mass spectrometric gas analyses. The author also wishes to thank Dr. Eugene R. Bissell for his helpful discussions. This work was sponsored by the U. S. Atomic Energy Commission.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Effect of Solutes on the Molecular Yields in the Radiolysis of Aqueous Solutions[1]

BY HAROLD A. SCHWARZ

RECEIVED APRIL 7, 1955

The molecular H_2 yield produced by γ-rays in KNO_2 and $CuSO_4$ solutions is found to decrease as the solute concentration is increased in the range of 10^{-5} to 1 molar. In $CuSO_4$ solutions, the Cu^{++} ion is the active species. Comparison of these data with published data on the effect of H_2O_2 on the H_2 yield and the effect of KBr and KCl on the molecular H_2O_2 yield shows that all of these yields *vs.* concentration curves coincide when the solute concentration is multiplied by a characteristic normalization constant. It is concluded that the mechanisms for formation of H_2 and H_2O_2 are similar as has been proposed by other authors. In the case of H_2 yields, the normalization factors are in the same ratio as the rate constants for reaction of H atoms with the solute wherever these are known. All of these results are consistent with the radical diffusion model in which H_2 and H_2O_2 are formed by combination of H and OH radicals as they diffuse out of a spur. A simple, approximate mathematical treatment of this model is given.

In the radiolysis of aqueous solutions by γ-rays, yields of H_2 and H_2O_2, called the molecular yields, are produced which are relatively independent of the nature of the solute.[2,3] Allen has ascribed these yields to the combination reactions of H and OH radicals as they diffuse away from the "hot spots" or "spurs" in which they are formed.[4] Samuels and Magee have attempted to calculate the magnitude of the yields to be expected from a radical diffusion model and find the model in agreement with the observed yields.[5]

On the basis of such a model, solutes that react with H atoms would be expected to lower the yield of H_2, and those that react with OH radicals would lower the H_2O_2 yield. The effect of solutes on the yield of H_2O_2 has been studied by several authors.[6-9] Hochanadel and Ghormley have studied the effect of H_2O_2 on the H_2 yield.[10] In the present paper, studies of the effect of KNO_2 and $CuSO_4$ on the H_2 yield are reported along with certain correlations that can be found among existing data.

Experimental

The preparation and analysis of the samples has been described elsewhere.[3] KNO_2 solutions were also examined for NO. A small known quantity of O_2 was added to the product gases in the analysis system. The pressure was noted before and several times after the O_2 was added. In the cases of the more concentrated KNO_2 solutions, a gas was present which spontaneously reacted with O_2 and froze out on liquid N_2. This gas was presumed to be NO.

Solutions were prepared with a known concentration of solute and then deaerated by boiling under vacuum. In most cases, portions of the solution were analyzed after deaeration. The concentration of the solute increased by approximately 5% during deaeration.

Results

The hydrogen yields, solution compositions and total doses are given in Tables I, II and III. All *G*

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

[3] H. A. Schwarz, J. P. Losee and A. O. Allen, *ibid.*, **76**, 4693 (1954).

[4] A. O. Allen, *Disc. Faraday Soc.*, **12**, 79 (1952).

[5] A. H. Samuels and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

[6] T. J. Sworski, THIS JOURNAL, **76**, 4687 (1954); *Radiation Research*, **2**, 26 (1955).

[7] F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.*, **49**, 1011 (1953).

[8] H. A. Schwarz and A. O. Allen, THIS JOURNAL, **77**, 1324 (1955).

[9] A. O. Allen and R. Holroyd, 127th National A.C.S. Meeting, 1955.

[10] J. A. Ghormley and C. J. Hochanadel, Radiation Research Society meeting, New York, N. Y., May 16, 1955.

TABLE I

H_2 YIELDS IN KNO_2 SOLUTIONS

$[KNO_2]$, M	Dose, e.v./l. $\times 10^{-21}$	G_{H_2}	$G_{NO} \times 10^2$
4×10^{-5}	1.84	0.449	..
4×10^{-5}	1.84	.437	..
4×10^{-5}	3.68	.435	..
1.2×10^{-3}	3.72	.417	0
1.2×10^{-3}	1.86	.401	0
1.2×10^{-3}	5.58	.407	0
1.2×10^{-2}	3.72	.356	0
1.6×10^{-2}	3.70	.362	0
1.6×10^{-2}	5.57	.352	0.2
5.8×10^{-2}	1.87	.320	0
5.8×10^{-2}	3.70	.324	0
5.8×10^{-2}	5.57	.316	..
0.165	1.96	.279	2.7
0.165	5.65	.269	2.4
0.394	1.98	.225	8.2
0.394	3.73	.226	7.9

TABLE II

H_2 YIELDS IN $CuSO_4$ SOLUTIONS

$[CuSO_4]$, M	$[Cu^{++}]$, M (calcd).	Dose, e.v./l. $\times 10^{-21}$	G_{H_2}
1.25×10^{-3}	1.0×10^{-3}	1.84	0.382
1.25×10^{-3}	1.0×10^{-3}	1.84	.381
1.25×10^{-3}	1.0×10^{-3}	3.69	.384
1.20×10^{-3a}	0.98×10^{-3}	3.76	.369
1.20×10^{-3a}	0.98×10^{-3}	5.74	.375
1.6×10^{-2a}	6.4×10^{-3}	3.76	.315
1.74×10^{-2}	6.8×10^{-3}	2.11	.321
1.74×10^{-2}	6.8×10^{-3}	5.17	.319
5.90×10^{-2}	1.4×10^{-2}	2.12	.290
5.90×10^{-2}	1.4×10^{-2}	5.20	.291
1.0	6.3×10^{-2}	6.61	.210
1.0	6.3×10^{-2}	9.77	.210
1.0	6.3×10^{-2}	12.10	.217

[a] These runs were 10^{-4} M in KBr.

TABLE III

H_2 YIELDS IN $CuSO_4$ SOLUTIONS CONTAINING H_2SO_4

$[CuSO_4]$, M	$[H_2SO_4]$, M	Dose, e.v./l. $\times 10^{-21}$	G_{H_2}
0^a	2.5×10^{-2}	1.80	0.452
0^a	2.5×10^{-2}	3.61	.447
0^a	2.5×10^{-2}	5.42	.442
1.21×10^{-3a}	2.5×10^{-2}	3.61	.441
1.21×10^{-3a}	2.5×10^{-2}	5.42	.442
1.65×10^{-2a}	2.5×10^{-2}	4.00	.358
1.65×10^{-2a}	2.5×10^{-2}	5.80	.363
0.55^a	2.5×10^{-2}	4.08	.244
0.55^a	2.5×10^{-2}	6.22	.257
1.2×10^{-3}	5×10^{-2}	3.61	.435
1.7×10^{-2}	5×10^{-2}	3.61	.389
1.7×10^{-2}	5×10^{-2}	5.41	.381
6×10^{-2}	5×10^{-2}	5.46	.326

[a] These runs were 10^{-4} M in KBr.

values (molecules produced per 100 e.v.) are based on a G for ferrous sulfate oxidation of 15.5.[11] The yields are all linear with dose. Johnson and Allen[2] have shown that 10^{-5} M KBr is sufficient to repress the reaction $OH + H_2 \rightarrow H_2O + H$. In the $CuSO_4$ solutions, the yields in the presence and absence of 10^{-4} M KBr are the same, hence the H_2 is protected from attack by OH radicals. It is seen that in all solutions, the H_2 yield decreases as the solute concentration increases. The H_2 yield in the absence of solute is taken to be the same as the yield in dilute KBr solutions, $G_{H_2} = 0.453$.[3,12] It has been shown by Hochanadel that increasing the KBr concentration above 10^{-6} M has little or no effect on the H_2 yield.[13]

In the more concentrated KNO_2 solutions a gas is produced which is believed to be NO (Table I). The yield of the gas is approximately proportional to the concentration of the solute and is of the right order of magnitude to be a direct effect.

In the case of $CuSO_4$, the addition of small amounts of H_2SO_4 (0.05 and 0.10 N) decreases the effectiveness of $CuSO_4$ in lowering the yield while the H_2SO_4 itself has little or no effect (Table III). Owen and Gurry have determined the dissociation constant of $CuSO_4$ to be 4.3×10^{-3}.[14] In a 1 M solution, the $CuSO_4$ is only 6% dissociated, while in a 10^{-3} M solution, it is 84% dissociated. The H_2SO_4 represses the dissociation of the $CuSO_4$, so it would appear that the Cu^{++} ion and not $CuSO_4$ is responsible for the effect on the H_2 yield. The calculated Cu^{++} concentrations are given in Table II. When H_2SO_4 is present the equilibria are rather complex and it is felt that calculated Cu^{++} concentrations would not be reliable.

Discussion

These hydrogen yields show the same type of slow variation with the solute concentration that was observed by Ghormley and Hochanadel[10] using H_2O_2 as the solute. Furthermore, the effect is similar to that noted by Sworski[6] in the H_2O_2 yields from acid Br^- solutions and Cl^- solutions and by Allen and Holroyd in neutral Br^- solutions.[9]

The H_2O_2 yield has also been studied in $FeSO_4$ solutions in 0.8 N H_2SO_4 by Dainton and Sutton[7] and in KNO_2 solutions by Schwarz and Allen.[8] As the $FeSO_4$ concentration is increased in the range of 10^{-6} to 10^{-4} M, the H_2O_2 yield falls slightly and the Fe^{++} oxidation yield increases markedly. These concentrations are three orders of magnitude smaller than concentrations showing effects in Br^- solutions. In the KNO_2 studies, the H_2O_2 yield decreases with increasing KNO_2 concentration, but appears to remain constant in the range of 10^{-3} to 10^{-2} M. These effects are not parallel to those observed in other solutions and probably have different causes.

All of the H_2 yields and the H_2O_2 yields in the Br^- and Cl^- solutions are shown in Fig. 1. G/G_0 is the ratio of the yield in the presence of solute at the specified concentration to the yield that would be observed if the solute had no effect (as obtained from Br^- solutions in the case of H_2 yields or from extrapolation to zero solute concentration in the cases of the H_2O_2 yields). [X] is a normalized concentration and is equal to the solute concentration multiplied by a normalization constant chosen for each solute to give the best agreement with other solutes. Two other systems have been in-

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[11] R. H. Schuler and A. O. Allen, private communication.

[12] A new calibration of the analysis system has resulted in raising the ratio of the H_2 yield to the Fe^{++} oxidation yield previously reported, by 1.7%.

[13] C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

[14] B. B. Owen and R. W. Curry, THIS JOURNAL, **60**, 3074 (1938).

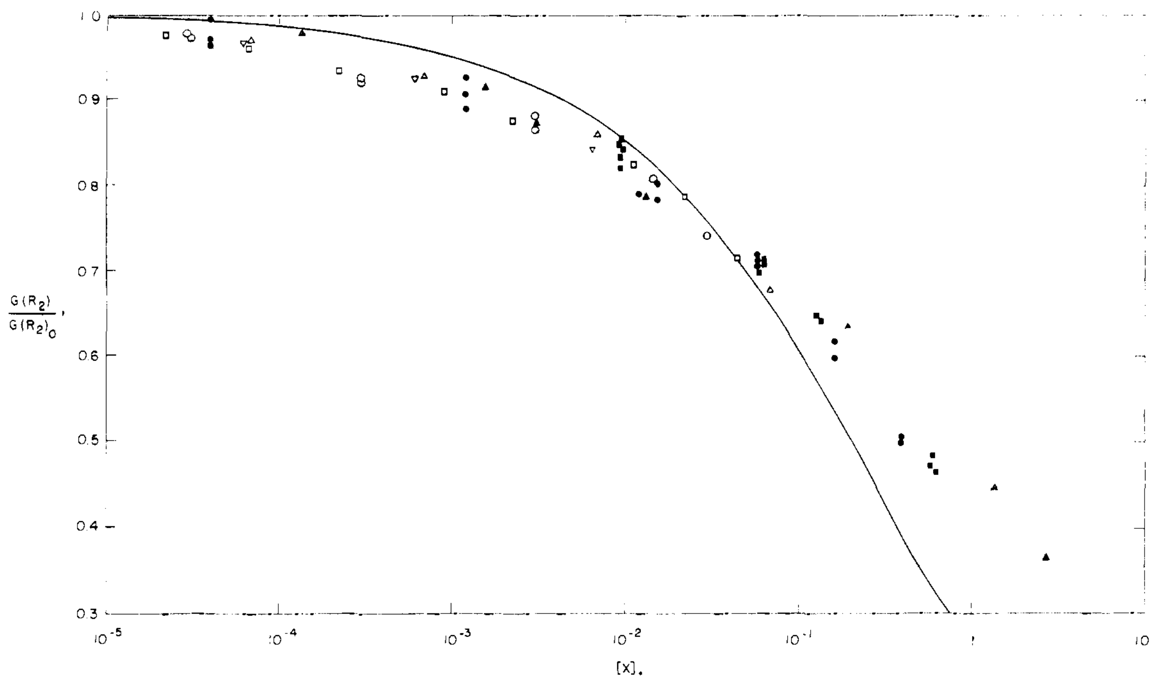

Fig. 1.—The effect of solute on the molecular yields of H_2 and H_2O_2. The solute concentrations are multiplied by a normalization factor to bring the curves into coincidence: ●, H_2 from KNO_2 solutions $[X] = [NO_2^-]$; ■, H_2 from $CuSO_4$ solutions, $[X] = 9.3\ [Cu^{++}]$; ▲, H_2 from H_2O_2 solutions (Hochanadel and Ghormley), $[X] = 1.9\ [H_2O_2]$; □, H_2O_2 from neutral KBr solutions (Allen and Holroyd), $[X] = 2.2 \times [Br^-]$; ○, H_2O_2 from KBr solutions both at *p*H 2 and 0.8 *N* H_2SO_4 (Sworski), $[X] = 3.0 \times [Br^-]$; △, H_2O_2 from KCl solutions in 0.8 *N* H_2SO_4 (Sworski), $[X] = 0.78$; ▽, H_2O_2 from KCl solutions, *p*H 2, (Sworski), $[X] = 7.4 \times 10^{-2}$. Curve is theoretical.

vestigated but have not yielded sufficient data to be included in Fig. 1. Ghormley and Hochanadel have determined the H_2 yield in O_2 saturated Br^- solutions ($\sim 1.4 \times 10^{-3}$ *M* O_2) and find $G/G_0 = 0.87$.[10] Hart has found that HCOOH does not affect the molecular H_2 yield in O_2 saturated solutions up to concentrations of 0.05 *M*.[15] From these results we find to a first approximation, the normalization constant for O_2 is 2 and for HCOOH is less than 0.04 times this, or less than 8×10^{-2}.

The correlation of the yields is very good and suggests that the H_2 and H_2O_2 are formed in kinetically similar processes. If the intermediates involved are H and OH radicals, as has been suggested by Allen and others,[4,5] then the normalization constants should have the same ratios as the rate constants for the reactions of the radicals with the solute. Although the information is meager, this comparison is possible in three cases of H_2 production and is given in Table IV. The good agreement would seem to favor the radical theory.

TABLE IV

COMPARISON OF NORMALIZATION CONSTANTS WITH RATE CONSTANTS FOR THE REACTION $H + X \rightarrow$ PRODUCTS

X	Normalization constant	Rate constants	
NO_2^-	1.0	. . .	
H_2O_2	1.9	$k_{H_2O_2}/k_{NO_2^-} = 2.1$	(8)
O_2	($\sim$2)	$k_{O_2}/k_{NO_2^-} \sim 1$	(8)
HCOOH	($<8 \times 10^{-2}$)	$k_{HCOOH}/k_{O_2} = 2 \times 10^{-3}$	(15)

The reactions $H + H \rightarrow H_2$ and $OH + OH \rightarrow H_2O_2$ cannot proceed homogeneously in the solutions. The percentage lowering of the yields changes from 10% at $[X] = 10^{-3}$ *M* to only 60% at 1 *M*. In the homogeneous case, a thousandfold concentration change would essentially stop the reactions to form H_2 and H_2O_2. However, H atoms are not present in uniform concentration throughout the solution. In the radiolysis of liquids, the energy release by the ionizing radiation is such that spurs are formed containing several ionizations or excitations in a radius of the order of 10 Å.[5,16] If the ionizing radiation is γ-rays or fast electrons, the spurs formed will be separated by several thousand Å. The H atoms must be formed in these spurs, so they are present in spots of high concentration that taper off to essentially zero concentration in the bulk of the solution.

No one has developed a rigorous mathematical treatment of diffusion kinetics that can be applied to the combination of radicals as they diffuse out from a spur. Samuels and Magee have developed the kinetics with the assumption that the radicals remain in a Gaussian distribution at all times.[5] The effect of solutes at low concentration on the probability of combination of two particles has been considered by Roy, Hamill and Williams[17] and by Noyes.[18] Fricke has extended the treatment of Samuels and Magee to the case where a solute is present, but the integrals involved present a formidable barrier to the calculation.[19] His cal-

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(15) E. J. Hart, THIS JOURNAL, **76**, 4312 (1954).

(16) D. E. Lea, "Actions of Radiations on Living Cells," Cambridge University Press, Cambridge, England, 1947.

(17) J. C. Roy, W. H. Hamill and R. R. Williams, THIS JOURNAL, **76**, 3274 (1954).

(18) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).

(19) H. Fricke, *Ann. N. Y. Acad. Sci.*, **59**, 567 (1955).

culations agree with the ones being presented here except that he calculates a smaller dependence at high solute concentration, in better agreement with the data.

A rather compact approximation to the kinetics may be made if it is assumed that when two radicals in a spur react, the total number of radicals in the spur is not changed. This is equivalent to calculating the effect of a reactive solute on the total number of encounters between radicals (if they did not react) as they diffuse out from a spur. The overlapping of two spurs in the track will be neglected since the spurs are so widely separated. The first part of the calculation is essentially the same as Samuels and Magee's.

The radicals referred to here are either H or OH radicals, whichever combination is being considered. If all of the radicals are initially formed at the origin of a system of spherical coordinates, then $W(r)\,\mathrm{d}v$, the fraction of the radicals which will be found in a volume element $\mathrm{d}v$ at a radius r and time t, is given by[20]

$$W(r)\,\mathrm{d}v = \frac{1}{(4\pi Dt)^{3/2}}\,e^{-r^2/4Dt}\,\mathrm{d}v$$

where D is the diffusion coefficient of the radicals. Since the radicals are not all formed at the origin, we assume that they are formed in a Gaussian distribution giving

$$W(r)\,\mathrm{d}v = \frac{1}{\{4\pi D(t+\tau)\}^{3/2}}\,e^{-r^2/4D(t+\tau)}\,\mathrm{d}v \qquad (1)$$

where τ is a constant representing the time it would have taken for the radicals to expand from a point to their initial distribution. The concentration of radicals at any radius is given by

$$[\mathrm{R}]_r = NW(r)$$

where N is the number of radicals in the spur. The rate of formation of the product, R_2, is given by the product of the concentration of the radicals times the concentration of $N - 1$ radicals times A, the rate constant for combination

$$\left(\frac{\mathrm{d}[\mathrm{R}_2]}{\mathrm{d}t}\right)_r = A[\mathrm{R}]_r[\mathrm{R}]_{r,N-1} = AN(N-1)W^2(r)$$

The rate of formation of R_2 molecules is found by integrating this equation over all space.

$$\frac{\mathrm{d}N(\mathrm{R}_2)}{\mathrm{d}t} = AN(N-1)\int_0^\infty W(r)^2\mathrm{d}v$$
$$= A'N(N-1)(t+\tau)^{-3/2} \qquad (2)$$

where $A' = (8\pi D)^{-3/2} A$ and $N(\mathrm{R}_2)$ is the number of R_2 molecules formed. Since we have assumed that the number of radicals in a spur does not change when two radicals react, all of the radicals will disappear by reaction with the solute.

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = \int_0^\infty B[\mathrm{R}]_r\,X\,\mathrm{d}v = BNX\int_0^\infty W(r)\,\mathrm{d}v = BNX$$

where B is the rate constant for the reaction of the radical with the solute and X is the solute concentration. Integrating this equation, we have the familiar expression

$$N = N_0e^{-BXt} \qquad (3)$$

where N_0 is the number of radicals initially present in the spur. Substituting equation 3 in equation 2

$$\frac{\mathrm{d}N(\mathrm{R}_2)}{\mathrm{d}t} = A'N_0e^{-BXt}\,(N_0e^{-BXt} - 1)(t+\tau)^{-3/2}$$

In order to obtain the total number of R_2 molecules produced in the spur, this equation must be integrated between $t = 0$ and the time at which only one radical is left, that is

$$N_0e^{-BXt_t} = 1$$

$$t_t = \frac{\ln N_0}{BX}$$

Hence the number of R_2 molecules produced in the spur is

$$N(\mathrm{R}_2) - A'\int_0^{\ln N_0/BX} N_0e^{-BXt}\,(N_0e^{-BXt} - 1)(t + \tau)^{-3/2}\,\mathrm{d}t$$

Making the substitution

$$Z = \{2BX(t+\tau)\}^{1/2}$$

and integrating by parts gives

$$N(\mathrm{R}_2) = 2A'N_0(N_0-1)\tau^{-1/2} - 2\sqrt{2}A'N_0(BX)^{1/2}e^{BX\tau}\left\{\sqrt{2}N_0e^{BX\tau}\int_{2(BX\tau)^{1/2}}^{2(\ln N_0 + BX\tau)^{1/2}} e^{-z^2/2}\,\mathrm{d}z - \int_{(2BX\tau)^{1/2}}^{(2\ln N_0 + 2BX\tau)^{1/2}} e^{-z^2/2}\,\mathrm{d}z\right\} \qquad (4)$$

In the absence of solute, $N = N_0$, and equation 2 gives an integration

$$N(\mathrm{R}_2)_0 = 2A'N_0(N_0-1)\tau^{-1/2} \qquad (5)$$

Dividing equation 4 by equation 5 we have

$$\frac{N(\mathrm{R}_2)}{N(\mathrm{R}_2)_0} = 1 - \frac{\sqrt{2}(BX\tau)^{1/2}e^{BX\tau}}{N_0-1}\left\{\sqrt{2}\,N_0e^{BX\tau}\int_{2(BX\tau)^{1/2}}^{2(\ln N_0 + BX\tau)^{1/2}} e^{-z^2/2}\,\mathrm{d}z - \int_{(2BX\tau)^{1/2}}^{(2\ln N_0 + 2BX\tau)^{1/2}} e^{-z^2/2}\,\mathrm{d}z\right\} \qquad (6)$$

However, τ is also a function of N_0. The average radius of the spur is

$$\bar{r} = \int_0^\infty rW(r)\,\mathrm{d}v = \left(\frac{16D(t+\tau)}{\pi}\right)^{1/2}$$

When $t = 0$

$$\bar{r}_0 = 4\left(\frac{D\tau}{\pi}\right)^{1/2} \qquad (7)$$

Magee has assumed that the initial volume of a spur is proportional to the number of radicals in the spur

$$\bar{r}_0^3 = N_0(\bar{r}_0')^3$$

From equation 7

$$\tau = N_0^{2/3}\tau'$$

Substituting this in equation 6

$$\frac{N(\mathrm{R}_2)}{N(\mathrm{R}_2)_0} = 1 - \frac{(2yN_0^{2/3})^{1/2}e^{yN_0^{2/3}}}{N_0-1}\left\{2^{1/2}N_0e^{yN_0^{2/3}}\int_{2(yN_0^{2/3})^{1/2}}^{2(\ln N_0 + yN_0^{2/3})^{1/2}} e^{-z^2/2}\,\mathrm{d}z - \int_{(2yN_0^{2/3})^{1/2}}^{(2\ln N_0 + 2yN_0^{2/3})^{1/2}} e^{-z^2/2}\,\mathrm{d}z\right\} \qquad (8)$$

where

$$y = BX\tau'$$

The integrals involved are found in tables of the normal probability function.[21] Values of $N(\mathrm{R}_2)/$

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(20) S. Chandrasekhar, *Rev. Modern Phys.*, **15**, 1 (1943).

(21) "National Bureau of Standards Applied Mathematics Series," Vol. 23 (U. S. Government Printing Office, Washington, D. C., 1953).

$N(R_2)_0$ for various values of y and N_0 are tabulated in Table V. $N(R_2)/N(R_2)_0$ is not strongly dependent on N_0 as can be seen from Table V. However, in order to calculate the variation in the actual R_2 yield, a spur size distribution is needed, along with the amount of R_2 produced in a spur of a given size. This information is given by Samuels and Magee to a reasonable approximation. $G_{R_2}/G^\circ_{R_2}$, the ratio of the observed R_2 yield to the R_2 yield at zero concentration of the solute, is given in the last column of Table V. This model predicts what is found experimentally, that the $G_{R_2}/G^\circ_{R_2}$ is dependent mainly on the concentration of solute and independent of the nature of R_2. Actually, the values would be different for H_2 and H_2O_2 since the number of molecules produced per spur is different in each case. However, in view of the small dependence on N_0, this effect is neglected.

TABLE V

CALCULATED VALUES OF $N(R_2)/N(R_2)_0$

	N_0					
y	2	4	6	10	20	$G_{R_2}/G^0_{R_2}$
10^{-4}	0.9604	0.9568	0.9534	0.9467	0.9339	0.955
10^{-3}	.8822	.8720	.8617	.8412	.8093	.864
10^{-2}	.6845	.6571	.6356	.5976	.5372	.642
10^{-1}	.3258	.3040	.2794	.2415	.1872	.288
2×10^{-1}	.2227	.2080	.1873	.1558	.1156	.192

In order to compare these kinetics with the experimental results, it is necessary to fix $B\tau'$. If $B\tau'$ is taken as 8×10^{-2} for NO_2^- solutions, the curve in Fig. 1 is obtained.

The agreement of the curve with the experimental data is quite good considering the approximations that were made. At high solute concentrations, most of the radicals do react with the solute, and the effect of the approximations on G_{R_2} is small. However the assumption that N does not vary as radicals combine makes $G^\circ_{R_2}$ too large. Hence the calculated $G_{R_2}/G^\circ_{R_2}$ should be too small.

At low solute concentration, the R_2 yield is still high, and both G_{R_2} and $G^\circ_{R_2}$ will be affected to about the same degree by this assumption. However, the assumption that combination of radicals does not affect the distribution will overemphasize the amount of combinations in the early stages and make the calculated G_{R_2} too large.

It remains to determine whether the magnitude found for the parameter $B\tau'$ is reasonable. The diffusion coefficient may be found in terms of the number of jumps a radical makes per second, n, and the mean square root path length of a jump λ.

$$D = 1/6n\lambda^2$$

From equation 7

$$D = \pi(\bar{r}_0')^2/16\tau'$$

If reaction occurs on every encounter in the solution, B will be given by the product of the number of jumps a radical makes per sec. and the amount of new "reaction volume" the radical sees per jump. The latter quantity will be given by the product of the cross section for reaction, σ, and the mean free path, l. Hence

$$B = n\sigma l$$

Combining the above quantities and equating l and λ as a first approximation

$$B\tau' = \frac{3\pi\sigma(\bar{r}_0')^2}{8l} \times \frac{N}{1000}$$

where N is Avogadro's number, and $N/1000$ is included to convert the constant to liters per mole per second. If σ is taken as $4\pi \times 10^{-6}$ cm.^{2}, $\bar{r}_0'$ as 6×10^{-8} cm. and l as 10^{-8} cm., then $B\tau' \cong 0.3$.

Values of $B\tau'$ for the various solutions in Fig. 1 are found by multiplying the normalization constant of the solute by 8×10^{-2}, the value of $B\tau'$ for NO_2^- solutions. They range from 6×10^{-4} to 0.74 and thus are all of the order of magnitude expected from a radical diffusion model.

Acknowledgment.—The author wishes to thank Dr. A. O. Allen for helpful discussions and criticism of this work.

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Isotopic Exchange Reactions of Neptunium Ions in Solution. III. The Effect of Chloride and Nitrate Ions on the Rate of the Np(V)–Np(VI) Exchange[1]

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RECEIVED APRIL 25, 1955

Possible catalytic effects of nitrate and chloride ions on the rate of the isotopic exchange reactions between Np(V) and Np(VI) have been investigated. Nitrate ion has little influence on the exchange rate. A marked catalysis is found in chloride solution. The results have been analyzed in terms of the formation of the complexes NpO_2Cl^+ and NpO_2Cl_2. Data are given on the energetics of the various exchange paths and for the formation of the complex species. Mechanisms for the exchange reaction are discussed.

A number of anionic complexing agents have been found to markedly affect the rate of isotopic exchange reactions between simple cations.[2] Determination of the exact role of the anion is of considerable interest. In certain cases where the ligand on the complex exchanges only slowly, it has been possible to demonstrate that a bridged activated complex is formed and that the ligand is transferred in the exchange process.[3–5] Net transfer of the ligand is not, however, a necessary feature of the electron transfer process.[5]

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] See, for example, J. Hudis and A. C. Wahl, THIS JOURNAL, **75**, 4153 (1953), and the systems cited therein.

[3] H. Taube and E. L. King, *ibid.*, **76**, 4053 (1954).

[4] H. Taube, H. Meyers and R. L. Rich, *ibid.*, **75**, 4118 (1953).

[5] H. Taube and H. Meyers, *ibid.*, **76**, 2103 (1954).