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Extremely Slow Reactions. I. The Isotopic Exchange Reaction between Iodobenzene and Potassium Iodide[1]

BY P. J. MANNO AND W. H. JOHNSTON

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The slow isotopic exchange reaction between iodobenzene and iodide ion was studied in a two phase system using I^{131} over the ranges of 16 to 46° and 10^{-4} to $10^{-1} f$ KI. The reaction, corresponding to exchange half-times up to 400 years, proceeded by a combination of a heterogeneous and a homogeneous mechanism. At low concentrations of KI the reaction was heterogeneous on glass and followed a Frumkin–Slygin competitive adsorption mechanism. At high concentrations the reaction was homogeneous and first order in iodide ion. Apparent activation energies were 10.7 and 3.7 kcal. mole^{-1} in the heterogeneous and homogeneous regions, respectively. Evidence indicated that the homogeneous reaction proceeded in the water phase with a frequency factor of 4.3×10^{-5} l. m.$^{-1}$ sec.$^{-1}$ corresponding to an apparent activation entropy of −80.6 e.u. mole^{-1} and, therefore, involved a complicated, highly solvated, activated complex.

Introduction

It is generally well known that radiochemistry has important applications to ordinary kinetics. It is less well known that the detection ability of modern low-level counting[2] extends the range of measurable kinetics to chemical half-times of millions of years or to the limit of the radiation induced reaction. The present paper reports the first of a series of slow reaction studies and treats the isotopic exchange reaction between iodobenzene and iodide ion in a two phase system using iodine-131 as a tracer.

In general aromatic nucleophilic substitutions of monohalogenated benzenes proceed slowly or apparently not at all.[3] Although various studies have been reported on the exchange reactions between iodide ion and organic iodides,[4] studies on the iodobenzene–iodide ion system have been restricted to elevated temperatures near 200°. The data are meager and reported to be difficult to reproduce and interpret.[4c,5] In the present study the kinetics are examined at an isotopic exchange half-time of nearly 400 years.

Experimental

Counting.—The determinations of the specific activities of iodine-131 were made by counting in iodobenzene with a low-level scintillation spectrometer.[2] Although comparable detection sensitivities can be obtained by low-level beta counting with either a "sandwich counter" or chemical sample conversion and a foil counter,[2] the use of a sodium iodide gamma detector simplifies sample handling with liquid samples. In this work the spectrometer was focused on the 364 kv. photopeak of the spectrum of the iodine-131. All counts on iodobenzene were referred to standard solutions of aqueous potassium iodide. Appropriate corrections were made for radioactive decay and for the relative counting efficiencies of iodobenzene and water.

Reagents.—The iodobenzene used was EK 152 obtained from Eastman Organic Chemicals, Rochester, New York, and was further purified by extractions with the wash-out solutions. The final purity was checked by comparison of the refractive index with the accepted literature value and was found to be within ±0.0001 refractive index units. The potassium iodide was reagent grade (M7326) obtained from Merck and Co., Inc., Rahway, New Jersey. A primary 1 *F* solution was made up in Normax volumetric flasks and subsequent dilutions were made with calibrated volumetric pipets. The flasks were wrapped in aluminum foil and frequently checked for decomposition of the iodide solutions. The sodium sulfite used in the washout process was reagent grade (M74301) and was obtained from Merck and Co., Inc., Rahway, New Jersey. Fresh solutions of 0.1 *F* sodium sulfite were made almost daily.

The radioactive iodine-131 was obtained as carrier free grade from the Oak Ridge National Laboratory, Oak Ridge, Tennessee, in the form of sodium iodide in basic sodium sulfite solution. From 0.5 to 2.0 millicuries of the radioactive iodine-131 were diluted to 25 ml. of the desired concentration of aqueous potassium iodide. Since the concentration of the iodine-131 was 5 to 20 mc. per ml., usually 5×10^{-3} to 50×10^{-3} ml. of the radioiodine solution was used in each dilution.

Procedure.—The present two phase system was made by mixing equal volumes of solutions of iodobenzene and aqueous potassium iodide at room temperature and maintaining suspension by shaking for various contact times. In later experiments the solutions were allowed to equilibrate in a constant temperature water-bath (maintained to ±0.02°) and then combined and stirred. The room temperature experiments agreed within experimental error with those carried out at 25.00 ± 0.02°. The method used for mixing the solutions had no effect on the reaction rate. After a given contact time a sample of iodobenzene was removed from the reaction mixture and washed with alternate washes of 0.1 *M* sodium sulfite and distilled water. All separations and washouts were made in the presence of red light, using a photographic safe-light. A 10-ml. aliquot was counted in a weighing bottle placed on the sodium iodide crystal in the mercury shield of the low-level scintillation spectrometer. After the gross specific activity of the iodobenzene was determined, usually to within a 1% standard deviation of counting, the iodobenzene was returned to the separatory funnel and the washing procedure repeated. A series of these washouts and counts was performed until the specific activity of the iodobenzene was constant as shown in Fig. 1. The aliquot of iodobenzene was returned to the reaction vessel and the process was repeated following appropriate additional contact times. Figure 1 shows the regular increase in specific activity of the washed aliquots with contact time.

In order to check the chemical identity of the iodine-131 in the iodobenzene, a fractional crystallization and a fractional distillation were performed. The results of both tests indicated that the iodine-131 was in the form of iodo-

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[1] (a) This work was supported in part by the United States Atomic Energy Commission under Contract No. At(11-1)-166 with Purdue University. (b) Taken in part from a thesis submitted by Peter J. Manno to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part before the Physical and Inorganic Division, The American Chemical Society, Dallas Meeting, April, 1956.

[2] (a) W. H. Johnston, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy," United Nations, New York, 1956, pp. 149–155; (b) W. H. Johnston, "Proceedings of the 2nd Symp. on Methods of Instrumental Analyses" (Sept., 1956); (c) W. H. Johnston, *Science*, **124**, 801 (1956).

[3] (a) C. I. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 797–815; (b) J. F. Burnett and R. E. Zahler, *Chem. Revs.*, **49**, 278 (1951).

[4] (a) A. C. Wahl and N. A. Bonner, editors, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 338–341; (b) R. D. Heyding and C. A. Winkler, *Can. J. Chem.*, **29**, 790 (1951); (c) S. May, A. Fava and B. Giraudel, *Compt. rend.*, **236**, 285 (1953); (d) D. J. Sibbett and R. M. Noyes, THIS JOURNAL, **75**, 761 (1953).

[5] (a) S. May, M. Sarof, A. Vobaure and P. Daudel, *Compt. rend.*, **233**, 744 (1950); (b) A. M. Kristjanson and C. A. Winkler, *Can. J. Chem.*, **29**, 154 (1951).

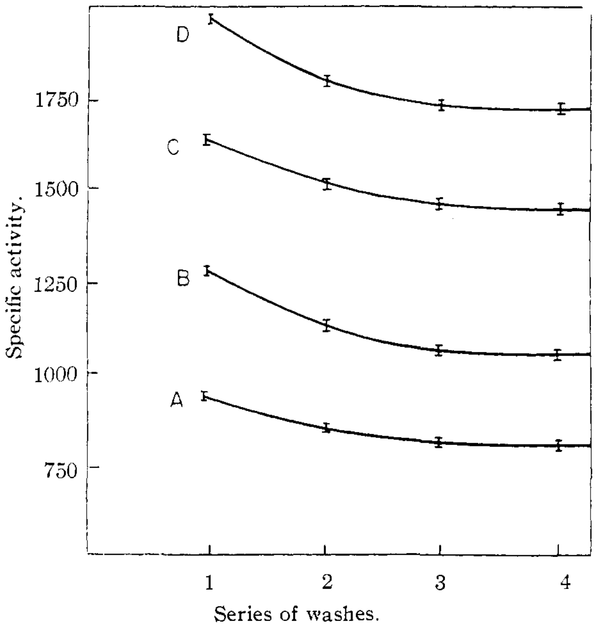

Fig. 1.—Relative specific activity (c. min.$^{-1}$ ml.$^{-1}$ × 5) as a function of series of washes for various contact times, where A, B, C, D are 21.5, 43.5, 67.5 and 89.5 hr., respectively.

131-benzene. The amount of iodine-131 was varied to investigate radiation catalysis.

Results and Discussion

Exchange Reaction.—A typical exchange study was run at a concentration of aqueous potassium iodide of 10^{-2} *F* at room temperature. The dependence of the specific activities of iodobenzene of Fig. 1 upon the time of contact is shown in Fig. 2.

For an extremely slow isotopic exchange reaction the usual first-order rate of approach to isotopic equilibrium[6] can be expected to be indistinguishable from a zero-order reaction for the time scale of the laboratory measurement. Thus the rate of isotopic change will be constant giving a linear relationship between the specific activity of a reactant and time from initial non-isotopic equilibrium. The expected linear relation is shown in Fig. 2.

The apparent zero-time exchange of Fig. 2 can be explained by a rapid transfer of radioiodine by reaction or exchange with a trace impurity in the iodobenzene. In Fig. 2 the extrapolation to zero time by the method of least squares corresponds to $1.63 \times 10^{-3}\%$ apparent exchange. This could be caused by as little as 2.0×10^{-7} mole fraction of appropriate impurity. When the iodobenzene was pretreated by shaking with a solution of inactive potassium iodide, the apparent zero-time exchange decreased. This indicated that some of the transfer of radioiodine was by chemical reaction as opposed to simple isotopic exchange with an impurity.

It was important to find out if the slow transfer of radioactivity to the iodobenzene was caused by

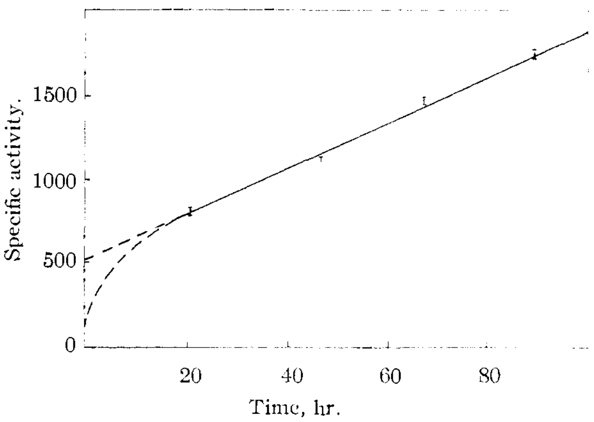

Fig. 2.—Change in the specific activity of the C_6H_5I with contact time.

a chemical reaction as opposed to the expected isotopic exchange reaction. In addition to the careful wash-out procedure, 20 ml. of the activated iodobenzene was fractionally crystallized as shown in Table I. It is apparent that the specific activities of the crystals and supernatants are constant with a satisfactory material balance. A similar check by fractional distillation also showed constant specific activity within experimental error.

TABLE I

INVESTIGATION BY FRACTIONAL CRYSTALLIZATION OF THE CHEMICAL FORM OF I^{131} TRANSFERRED TO IODOBENZENE

Fraction[a]	Fraction, ml.	Spec. act. (c./m./ml.)	Total act. (c./m.)	% Act. balance
0	20.0	2512 2500	Av. 50,120	
				97.6
S-1	10.4	2491	25,906	
C-1	9.6	2395	22,992	
				101.0
S-2	6.0	2495	14,970	
C-2	3.6	2459	8,852	
				100.0
S-3	1.3	2493	3,241	
C-3	2.3	2466	5,672	
			Av.	99.5

[a] O, original; S, supernatant; C, crystals.

The question of radiation catalysis in this reaction was investigated by varying the amount of iodine-131 per series by a factor of almost 14. The results are shown in Table II in which, for each

TABLE II

INVESTIGATION OF RADIATION CATALYSTS OF THE EXCHANGE REACTION

I^{131},[a] millicuries	KI, *F*	Isotopic exchange constant[b]	Rate of exchange[c]	Ratio of rates[d]
0.15	10^{-4}	28.8	2.88	1.5
0.41	10^{-2}	0.645	6.45	1.2
1.14	10^{-2}	0.511	5.11	1.0
1.58	10^{-4}	18.9	1.89	1.0
2.05	10^{-4}	26.7	2.67	1.4

[a] At the time of mixing. [b] Units of hr.$^{-1}$ × 10^6. [c] Units of moles liter^{-1} hr.$^{-1}$ × 10^9; last digit not significant. [d] Observed to expected (Table III).

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[6] (a) H. A. C. McKay, *Nature*, **142**, 997 (1938); (b) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946); (c) H. T. Norris, *J. Phys. Colloid Chem.*, **54**, 777 (1950); (d) G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).

series, the linear change in the specific activity of the iodobenzene with time following the initial apparent zero-time exchange is expressed as the rate of fractional approach to isotopic equilibrium in reciprocal hours. Each series represents 3 to 6 experimental points at different contact times. These data do not show a dependence on the radiation of the iodine-131.

Concentration Studies.—The dependence of the rate of exchange upon the concentration of aqueous potassium iodide was measured from 10^{-4} to 10^{-1} F in borosilicate glass at room temperature. The isotopic exchange constants, k, for each experiment were calculated by the relation

$$k = \frac{A - A_0}{(A_\infty - A_0)t} \qquad (1)$$

where A^0, A and A_∞ are the specific activities of iodobenzene at zero-time, at time, t, and at complete isotopic equilibrium. The apparent zero-time exchange was obtained from a least squares plot of the data of each series. For a very slow reaction the term $(A - A_0)/(A_\infty - A_0)$ is the fraction exchanged. The usual expression for the rate of total exchange[6]

$$R = \frac{k(C_6H_5I)(I^-)}{(C_6H_5I) + (I^-)} \qquad (2)$$

was used.

The data of these concentration studies are summarized in Table III which shows the concentration of KI, the average isotopic exchange constant, and the rate of exchange, R. The average isotopic exchange constants were obtained by the method of least squares from the data of each series as illustrated in Fig. 2.

The complex rate dependence shown in Table III can be explained as a combination of heterogeneous and homogeneous reactions. The initial rapid rise and decline suggests the Langmuir–Hinshelwood competitive adsorption mechanism.[7] In this interpretation the subsequent first-order dependence of rate upon concentration is the region of the homogeneous mechanism following poisoning of the surface reaction by excess potassium iodide.

TABLE III

THE EFFECT OF THE CONCENTRATION OF AQUEOUS POTASSIUM IODIDE ON THE RATE OF EXCHANGE WITH IODOBENZENE

KI, F	Av. isotopic exchange constant[a]	Rate[b] of exchange of series
1.0 × 10^{-4}	26.68	2.67
	16.82	1.68
	22.69	2.27
	19.63	1.96
	14.41	1.44
	18.94	1.89
	11.56	1.16
1.0 × 10^{-3}	7.084	7.08
2.0 × 10^{-3}	9.718	19.4
	8.719	17.4
3.0 × 10^{-3}	4.692	14.1
5.0 × 10^{-3}	2.551	12.8
7.1 × 10^{-3}	1.280	9.09
1.0 × 10^{-2}	0.6446	6.45
	.4535	4.53
	.5113	5.11
	.4943	4.94
	.5786	5.79
5.0 × 10^{-2}	.2263	11.3
1.0 × 10^{-1}	.2151	21.5

[a] In hr.$^{-1}$ × 10^6; 3 to 6 exp. points per series; last two digits not significant. [b] In moles l.$^{-1}$ hr.$^{-1}$ × 10^9; last digit not significant.

As a check on this interpretation, several exchange series were done at 10^{-4} F KI in polyethylene, fluorocarbon and packed glass vessels at 25.0°. The average rates of exchange in moles l.$^{-1}$ hr.$^{-1}$ × 10^9 were 1.05, 0.52 and 43.7, respectively. These rates are to be compared with 2.0 in glass as shown in Table III. On the other hand a fluorocarbon series at 5 × 10^{-2} F KI was within experimental error of the rate in glass. Thus the rates of exchange on these surfaces also indicate the heterogeneity of the reaction at low concentration of potassium iodide.

In order to investigate the possible catalysis of traces of dissolved oxygen or iodine, two series were run with 10^{-6} F I_2 and with careful degassing with oxygen-free nitrogen at 10^{-4} and 10^{-1} F KI, respectively. No catalysis was observed. The added iodine somewhat slowed the heterogeneous reaction and the removal of oxygen had little effect upon the homogeneous reaction. It is not unreasonable that the added iodine partially poisoned the glass surface in the same manner as excess potassium iodide.

Apparent Activation Energies.—The temperature coefficients of rate of exchange were measured from 16.0 to 46.0° for the heterogeneous and homogeneous reactions at 2.0 × 10^{-3} and 5.0 × 10^{-2} F KI, respectively. These data are summarized in Table IV. Arrhenius activation energy plots of the isotopic exchange constants give straight lines corresponding to apparent activation energies of 10.7 and 3.7 kcal. mole^{-1} for the heterogeneous and homogeneous reactions, respectively. The data at 2 × 10^{-3} F KI were taken in glass flasks of a different shape from those used for Table III. Although the rates are not strictly comparable, the region is still predominantly heterogeneous.

TABLE IV

DATA SHOWING THE EFFECT OF TEMPERATURE ON THE RATE OF EXCHANGE

Region	Temp.,[a] °C.	Av. isotopic exchange constant[b]	Rate of exchange[c]
Heterogeneous	16.00	2.368	4.74
(2 × 10^{-3} F KI)		2.508	5.16
	31.00	4.808	9.62
		5.090	10.2
	46.00	18.34	36.7
		16.03	32.1
Homogeneous	16.00	0.1803	9.02
(5 × 10^{-2} F KI)	25.00	.2263	11.3
	46.00	.3337	16.7

[a] ±0.02°. [b] Units of hr.$^{-1}$ × 10^6; last two digits not significant; at least 3 runs per series. [c] Units of moles l.$^{-1}$ hr.$^{-1}$ × 10^9; last digit not significant.

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[7] (a) I. Langmuir, *Trans. Faraday Soc.*, **17**, 621 (1921); (b) C. N. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, New York, N. Y., 1940, p. 178; (c) R. M. Adams, R. B. Bernstein and J. J. Katz, *J. Chem. Phys.*, **22**, 13 (1954).

Rate Laws and Mechanisms.—If the slow isotopic exchange of iodobenzene and iodide ion is the sum of a heterogeneous competitive adsorption reaction and a homogeneous reaction which is the expected S_N2 reaction, then the total rate, R, when the concentration of iodobenzene is constant, may be expressed as[7]

$$R = \frac{k_1A}{(1 + k_2A)^2} + k_3A \qquad (3)$$

where A is the concentration of aqueous potassium iodide and k_1, k_2 and k_3 are constants made up of the true specific rate constants, the adsorption coefficients of iodobenzene and iodide ion (or potassium ion), the constant concentration of iodobenzene, and the partition coefficients for the solute phase in the solvent phase.

If the data of Table III are compared with eq. 3, it is seen that the agreement is only very approximate in the region of the Langmuir–Hinshelwood decrease in rate.

On the other hand a competitive adsorption mechanism may proceed through an alternative adsorption isotherm. In cases where the Langmuir isotherm was not applicable, Temkin and Pyzhev[8] have successfully used the isotherm of Frumkin and Slygin.[8b,9] Using this isotherm for two components, A and B, in competitive adsorption, the rates of adsorption, r_a, and desorption, r_d, may be expressed for one of the species, A, as

$$r_a = k_A(\mathrm{A})e^{-g(a+b)} \qquad (4)$$

and

$$r_d = k_{-A}\,e^{ha} \qquad (5)$$

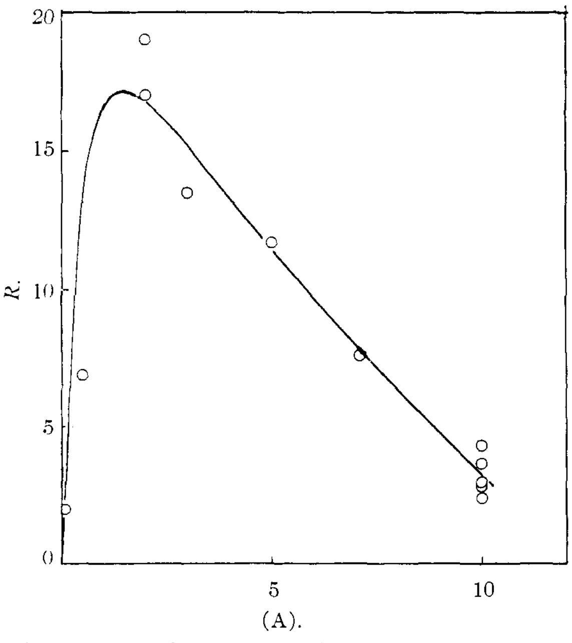

Fig. 3.—Rate of exchange, R in mole l.$^{-1}$ hr.$^{-1}$ $\times$ 10^9, *versus* concentration of KI, (A) in mole l.$^{-1}$ $\times$ 10^{-3}. The solid curve is the Frumkin–Slygin competitive adsorption kinetics.

where a and b are the surface concentrations of A and B, respectively, (A) is the concentration of A, and k_A, k_{-A}, g and h are constants. Using eq. 4 and 5 for both species, the expression for the rate, R, of a bimolecular surface reaction where the concentration of one of the species, B, is constant, as in this case, becomes

$$R = k_1 + k_2 \ln(\mathrm{A}) - k_3\,\overline{\ln(\mathrm{A})}^2 \qquad (6)$$

where k_1, k_2 and k_3 are constants made up of the constants of eq. 4 and 5 and the specific rate constant of the surface reaction. Equation 6 is the Frumkin–Slygin analog of the Langmuir–Hinshelwood competitive adsorption kinetics for one varying concentration.

In Fig. 3 this equation is compared with the data of Table III in the region of heterogeneity. Corrections were made for the first-order rate of the homogeneous reaction using the observed dependence of 0.211 hr.$^{-1}$ for concentration in moles l.$^{-1}$ $\times$ 10^3 of aqueous potassium iodide and rate of exchange in moles l.$^{-1}$ hr.$^{-1}$ $\times$ 10^9. As shown in Fig. 3 the Frumkin–Slygin competitive adsorption kinetics reasonably fit the experimental data. For R and (A) in the units above, the constants k_1, k_2 and k_3 of eq. 6 are 16.7, + 6.18, and 19.6, respectively, using logarithms to the base 10.

It is interesting to consider the phase in which the homogeneous exchange reaction is taking place. This problem may be approached by a comparison of the frequency factors calculated for each phase as the solvent. These calculations were done for a concentration of 0.020 F KI where the rate of exchange of the homogeneous reaction was $1.17_2 \times 10^{-12}$ moles l.$^{-1}$ sec.$^{-1}$.

Assuming the exchange reaction to occur to the iodobenzene it is necessary to know the partition of KI between this solvent and water at an aqueous concentration of 0.02 F. This partition was measured by Liu and corresponds to a concentration of 3.59×10^{-3} mole l.$^{-1}$ in the iodobenzene.[10] Using the measured value for the apparent activation energy, which takes into account the change in partition with temperature, the frequency factor is 1.81×10^{-8} l. mole^{-1} sec.$^{-1}$ for the iodobenzene phase. Assuming reaction in the aqueous phase and using the measured value of 6.8×10^{-4} mole l.$^{-1}$ for the solubility of iodobenzene in water, the frequency factor is 4.28×10^{-5} l. mole^{-1} sec.$^{-1}$ for the water phase.

Despite the slowness of this reaction which corresponds to an exchange half-time of approximately 390 years, the larger frequency factor is more reasonable. It is, therefore, probable that this reaction occurred in the water phase.

The frequency factor of 4.28×10^{-5} l. mole^{-1} sec.$^{-1}$ corresponds to an apparent entropy of activation of -80.6 e. u. mole^{-1} for a standard state of 1 mole per liter.[11] It is clear that the slowness

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[8] (a) M. Temkin and V. Pyzhev, *Acta Physicochim. U.R.S.S.*, **12**, 327 (1940); (b) K. J. Laidler, "Catalysis," edited by P. H. Emmett, Reinhold Publ. Corp., New York, N. Y., 1954, p. 142.

[9] A. Slygin and A. Frumkin, *Acta Physicochim. U.R.S.S.*, **3**, 791 (1935).

[10] This partition was measured recently using I^{131} by Mr. David Liu who is continuing the study of this exchange reaction in single phase systems.

[11] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 199, 417.

of this reaction is due to a large entropy of activation involving a complex orientation and solvation of the activated complex[12] and probable solvation of the iodobenzene in water in the manner of Baker's observations of 12 water molecules per molecule of octadecane in water.[13]

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[12] W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 497 (1935).

[13] E. G. Baker, "Symposium on Chemistry in the Exploration and Production of Petroleum," American Chemical Society, Dallas Meeting, April, 1956.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Chemical Aspects of the Geiger–Müller Discharge. II. The 2-Propanol–Argon Counter[1]

BY ROBERT W. KISER AND W. H. JOHNSTON

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The decomposition of 2-propanol quench gas by the Geiger–Müller discharge in an argon counter was investigated mass spectrometrically. Decomposition is essentially first order with a decomposition constant of 2.63 × 10^{-9} per pulse. The stoichiometry for the observed decomposition of 2-propanol may be approximated by $14CH_3CH(OH)CH_3 = 9CH_3CH_2OH + 8CH_3CHCH_2 + 5H_2O$. The primary mechanism of decomposition is attributed to electron impact in the gas phase. The specific electron yield is determined for 2-propanol and compared with the previously studied case of ethanol.

Introduction

In an attempt to elucidate the chemical reactions and the kinetics of decomposition of the quenching agent in a Geiger–Müller counter, Kiser and Johnston recently reported a study of the ethanol–argon counter.[2] Of the three mechanisms postulated, the primary mechanism of decomposition was that of electron impact in the gas phase.

It is of interest to know whether this mechanism also is dominant for other quenching agents. The present work describes a study of the decomposition of the quenching agent 2-propanol, where it is evidenced that the electron impact mechanism still predominates. The 2-propanol decomposition in argon has a first-order decomposition constant of 1.17 × 10^{-18} per electron.

The effective electron yield of the decomposition of 2-propanol and of the previous case of ethanol were recalculated in the form of specific electron yields for decomposition. A simple qualitative explanation is given for the difference between these yields.

Experimental

A Geiger–Müller counter with an internal silver cathode was filled to a partial pressure of 9.1 mm. with 2-propanol vapor and to a partial pressure of 82.9 mm. with argon (Matheson). The 2-propanol previously had been purified by repeated freezing and evacuation. This counter was then fitted directly to the front manifold of a modified model 21-201 Consolidated Electrodynamics Corporation mass spectrometer. The modifications of the mass spectrometer employed have been described previously.[2]

The source of radiation was cobalt-60 of approximate strength of 10 microcuries, placed 2.5 cm. distant from the counter wall. The count rate was approximately 2 × 10^4 counts per minute. Two ordinary scalers in series were used to record the pulses of the Geiger–Müller tube, the first acting as the usual scaler and the second as the register. The gas was admitted to the mass spectrometer at varying times and analyzed at a constant manifold pressure. Because of time limitations during analyses, the region observed ranged from *m/e* 19 to *m/e* 59. The results of these determinations are given in Table I.

Although the mechanism does not appear to be the same for the methane counter,[3,4] it is possible that the electron impact mechanism may operate in the case of ethyl acetate.[4,5,6]

TABLE I

MASS SPECTRAL DATA FOR THE DECOMPOSITION (CORRECTED), VALUES IN MILLIVOLTS

Counts × 10^{-6} *m/e*	0	8.76	20.2	32.9	56.2	68.0	68.8
20	33.3	34.3	36.4	35.2	35.8	38.3	43.5
26	0.51	0.36	0.32	0.36	0.38	0.39	0.44
27	1.96	1.86	1.55	1.66	1.58	1.58	1.94
28	4.48	3.50	3.23	3.48	3.60	3.96	5.15
29	0.93	0.80	0.80	0.72	0.72	0.76	0.90
31	.81	.53	.52	.57	.54	.64	.71
32	.00	.11	.08	.06	.05	.03	.05
39	1.03	.88	.83	1.00	1.04	1.07	1.24
40	119.0	125.0	119.9	125.4	124.9	129.0	147.0
41	1.35	1.12	1.12	1.26	1.33	1.36	1.60
43	1.20	1.09	0.95	1.01	1.04	1.07	1.21
44	0.31	0.28	0.23	0.25	0.21	0.26	0.30
45	5.31	4.47	4.17	4.43	4.19	4.13	4.69

For maintenance of a continual check on the sensitivity of the mass spectrometer during these analyses, a reference gas mixture composed of argon, ethene, ethanol and 2-propanol also was analyzed regularly. The seven analyses performed on the synthetic reference gas mixture agreed to within 4%, the major peaks having only a disagreement of 1 to 1.5%. The argon content of the counter remained constant to within 1%. The analysis of the synthetic gas mixture agreed to within an average deviation of about 5% from the manometric data obtained from the blending process. By a comparison of each individual analysis of the reference gas mixture with the average of all such analyses, values were obtained with which to correct the mass spectrum of each analysis of the 2-propanol–argon counter filling. This compensated for the greatest part of noted fluctuations in the mass spectrometer during analyses. To obtain calibrations, the pure gases and vapors were analyzed separately.

By means of the technique described in the earlier work on ethanol,[2] it was found that (2.25 ± 0.13) × 10^9 electrons are passed in each pulse counted in the 2-propanol–argon counter.

Analysis of Spectral Data.—The detailed method for the determination of the composition from the mass spectral

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[1] (a) This work was supported in part by the United States Atomic Energy Commission under Contract No. At(11-1)-166 with Purdue University. (b) Taken in part from work in progress for a thesis to be submitted by Robert W. Kiser to the Graduate School of Purdue University in partial fulfillment of the requirements for the Ph.D. degree.

[2] R. W. Kiser and W. H. Johnston, THIS JOURNAL, **78**, 707 (1956).

[3] E. C. Farmer and S. C. Brown, *Phys. Rev.*, **74**, 902 (1948).

[4] S. S. Friedland, *ibid.*, **71**, 377 (1947).

[5] S. S. Friedland, *ibid.*, **71**, 898 (1948).

[6] S. S. Friedland and H. S. Katzenstein, *ibid.*, **84**, 591 (1951).