π-electrons on the oxygen will be mentioned. First to be considered is the complicated structure which overlaps the NV_1 bands over their entire breadth. According to the plan summarized in Fig. 3 the $n\pi$-transition (p_0,π_-) should be in the NV_1 region but it is clearly impossible to pick any one part of the NV_1 band as being $n\pi$ on the basis of structure alone. In fact the various maxima in the broad NV_1 region surely represent vibronic details and possible Rydberg transitions.

An interesting effect may sometime be observed related to the (assumed) approximate equality of the energies of the p_0- and π_0-orbitals. The states of the molecule which are considered to be represented fairly accurately by wave functions based on the configurations

$$\pi_+{}^2\ \pi_0{}^1\ p_0{}^2\ \pi_-{}^1 \quad (V_1)$$

and

$$\pi_+{}^2\ \pi_0{}^2\ p_0{}^1\ \pi_-{}^1$$

are approximately degenerate so that, for example, the lifetime of the V_1 state might be abnormal.

Also by reason of the equality of the n- and π-energies, there is an uncertainty in assigning the Rydberg limit as the π-electron or lone-pair ionization potential.

It is believed that the spectra together with the interpretation given will be found typical of other simple amides, and in fact of many other systems which consist of four π-electrons in three π-orbitals (esters, oximes, etc.).

Seattle, Washington

[Contribution from the Department of Chemistry, Cornell University]

Hydrogen Isotope Exchange between Anthracene and Sulfuric Acid[1]

By V. Gold[2] and F. A. Long

Received May 14, 1953

The hydrogen isotope exchange between sulfuric acid and anthracene proceeds more rapidly at the *meso*-positions than at the other positions of anthracene. The kinetics of deuterium loss from the 9-position of anthracene by the action of sulfuric acid have been followed by experiments on the two-phase system, carbon tetrachloride–sulfuric acid. The velocity of the exchange reaction increases steeply with acidity. Analysis of the kinetic results, based on a model of the reaction which associates the yellow color of a solution of anthracene in sulfuric acid with a conjugate acid of anthracene in which a proton is added at a *meso*-position, leads to a value for the rate constant of proton loss from this conjugate acid. The rate of the proton loss decreases with acid concentration, and the rate of proton addition to anthracene appears to be insensitive to the composition of the acid in the range 84–90% H_2SO_4 by weight.

Exchange reactions of the type

$$C_6H_6 \xrightarrow{D^+} C_6H_5D + C_6H_4D_2,\ \text{etc.}$$

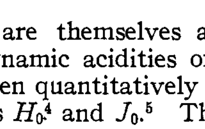
and

$$C_6H_5D \xrightarrow{H^+} C_6H_6$$

represent probably the simplest examples of aromatic substitution. It was established a number of years ago[3] that the isotope exchange between benzene derivatives and sulfuric acid-D_2 followed the known rules for electrophilic aromatic substitution reactions, as regards the dependence of orientation and reaction velocity on the nature of substituent groups already present in the benzene ring. At the same time it was qualitatively shown that the potency of an acid reagent depended on what was termed its "hydrion donating power."

There are other electrophilic aromatic substitution reactions, *e.g.*, nitration, for which the rate is governed by the "hydrion donating power" (or acidity) of the reaction medium. A distinction must, however, be made between these two cases. In the isotope exchange reaction a "kinetic acidity"—which will depend on the *rate* of proton (or deuteron) transfer reactions—is involved; in the latter case the term "acidity" is understood to mean the thermodynamic solvent property which controls the *equilibrium* concentrations of some reagent species (which are themselves acidic or basic). These thermodynamic acidities of strongly acidic solvents have been quantitatively described by the acidity functions H_0[4] and J_0.[5] There has been no corresponding analysis of the "kinetic acidity" of an acid solvent system.

The present study is concerned with the isotope exchange between anthracene and sulfuric acid in a stirred two-phase system, carbon tetrachloride being used as solvent for anthracene. The kinetics of the reaction under these conditions can be analyzed in some detail since the distribution of anthracene between the two phases can be measured independently by ultraviolet spectrophotometry. The particular choice of anthracene arose out of earlier experiments[6] in which it was found that anthracene is soluble in concentrated sulfuric acid with the formation of a species having a different ultraviolet absorption spectrum (and a yellow color) and to which the structure



I

was assigned on the basis of its absorption spectrum. In all experiments with anthracene and sulfuric acid, a certain amount of loss of anthracene through

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[1] Presented in part at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

[2] du Pont Grant-in-Aid Fellow at Cornell, 1951–1952.

[3] C. K. Ingold, C. G. Raisin and C. L. Wilson, *Nature*, **134**, 734 (1934); *J. Chem. Soc.*, 915, 1637 (1936).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. IX.

[5] V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951).

[6] V. Gold and F. L. Tye, *ibid.*, 2172, 2184 (1952).

sulfonation occurred. However, we found, as in the experiments with benzene,[3] that the velocity of sulfonation is less than that of the exchange.

Experimental

Isotopic Analysis.—(a) Absolute assay: 10-mg. samples of the organic compound were burnt according to standard microanalytical procedure. The combustion water was collected in a trap by condensation at −80° and then reduced to hydrogen by uranium metal at 400°.[7] The gas samples were analyzed by mass spectrometer at Brookhaven National Laboratory. We are indebted to Dr. L. Friedman for assistance in the analyses.

(b) Deuterium content at the *meso*-positions of anthracene: The anthracene sample was quantitatively oxidized by acid dichromate[8] (with loss of the hydrogen atoms of the *meso*-positions) and the deuterium content of the resulting anthraquinone was determined as above. It was verified that the conditions of oxidation employed did not induce significant isotope exchange.

(c) Relative abundance of anthracene-D_1, -D_2, -D_3, etc.: A procedure for the direct mass spectrometric analysis of anthracene vapor (scanning the region of mass 178 upwards) was developed by Friedman[9] and a few of our specimens were analyzed by him by this method.

(d) Analysis by infrared spectrophotometry: It was found even for samples with a low over-all deuterium content that several strong absorption bands (not present in ordinary anthracene) could be observed in the wave length region 9–15 μ. It was also found that the intensities of several strong bands in this region (*e.g.*, at 10.00 and 10.50 μ) were independent of the deuterium content of the sample. It seems likely that the former bands are due to C–H rocking vibrations and the latter to skeletal vibrations. Furthermore, using the results of method (c) we infer in particular that the bands at 11.86 and 12.68 μ are characteristic of 9-anthracene-D_1, and the bands at 12.79 and 14.69 μ of 9,10-anthracene-D_2. Using synthetic mixtures and other anthracene specimens the deuterium contents of which were established by method (a), an empirical equation was derived

$$\%\ \text{anthracene-D}_1 = \text{const.} \times \frac{\log (T_{12.68}/T'_{12.68})}{\log (T_{10.00}/T'_{10.00})} \times \left(0.86 + 0.48 \log \frac{T_{10.00}}{T_{10.00}}\right)$$

where T_λ is the percentage transmission at the wave length λ, and T'_λ that of the base line at the same wave length, relating the ratio of the logarithms of the intensities of the absorption bands at 12.68 and at 10.00 μ to the deuterium content. The use of the internal standard (10.00 μ band) obviated the need for accurate control of concentrations in the absorption cell, although the second term of the equation is a concentration-dependent correction which was required to allow for the observed deviation from Beer's law. Expressed as over-all percentage deuterium content, the reliability of this analytical procedure was ±0.1% D over the range 0–3% D.

The infrared measurements were taken on solutions of anthracene in CS_2 with a Perkin-Elmer D21 double-beam instrument using a pair of rock salt cells of 1 mm. path length.

Introduction of Deuterium into Anthracene.—(a) By the reaction between anthracene and sulfuric acid-D_2: A saturated solution of anthracene in CCl_4 (1.25 liters) was shaken with a small volume (20 ml.) of sulfuric acid-D_2 (1.25 D_2O/SO_3). The analytical figures for two of the samples prepared by this method (XI and XII) are given in Table I. The large proportion of highly deuterated species in the specimen suggests that the agitation was inadequate to ensure equilibrium in the distribution of anthracene between the two phases. During the early stages of the exchange the ratio (D in 9,10-positions)/(D in 1,2-positions) should approximate to the ratio of the rate constant for isotope exchange at a *meso*-position to the *average* rate constant (per position) at the 1,2-positions. This would mean that, according to what the (unknown) value of the ratio of the reactivities of the 1- and 2-positions is, a *meso*-position is roughly between 8 and 16 times more reactive than the next most reactive position. Because of the high proportion of anthracene-D_2 this is to be regarded as a *minimum* value. Experiments on the rate of loss of deuterium from a deuteroanthracene specimen prepared by this method again suggest that the ratio of the rate of loss of deuterium from one of the most reactive positions to the rate of loss from one of the next most reactive positions is roughly between 10 and 20. This means that the rate of deuterium introduction or the rate of loss of deuterium from a specimen prepared by this method would have to be analyzed in terms of at least two and, possibly three, different rate constants corresponding to the three groups of non-equivalent hydrogen atoms in anthracene. This method of preparation was therefore not investigated further.

Table I

Analytical Figures for Deuterated Anthracene Specimens

No.	Method of prep.	D, %[a]	% D in 9,10-positions[b] / % D in 1,2-positions	Percentage total deuterium as[c] Anthracene -D_1	-D_2	-D_3	-D_4	-D_5
XI	a	1.54	14 ± 2	..	..	..	..	..
XII	a	3.29	18 ± 2	16	48	23	11	3
X	b	2.89	∞	80	20	0	0	0

[a] Analysis method (a). [b] Analysis method (b). [c] Analysis method (c).

(b) By the reduction of anthrone: Anthrone was reduced to anthracene essentially according to the procedure of Martin,[10] the only modification being the use of a smaller volume of a mixture of D_2O and H_2O (1:3) instead of water. Deuterated anthracene (violet fluorescence) was obtained in 70% yield (specimen X; analytical figures in Table I). This specimen was used in the main series of kinetic experiments.

Kinetic Experiments on the Loss of Deuterium from the *meso*-Positions.—A measured volume of sulfuric acid (25 ml. as a rule) was added to a solution of deuterated anthracene (X) in CCl_4 (50 ml., $^1/_{200}$ M approx., as a rule) in the reaction flask. The two-phase system was agitated by a rapid rotary stirrer without exposing the contents of the flask to the atmosphere. After a timed interval, the stirring was stopped and the layers separated as far as possible by decantation and, if necessary, by centrifuging for a fraction of a minute. The carbon tetrachloride layer was shaken with and then allowed to stand over calcium oxide for several hours, after which the solution was filtered, and the carbon tetrachloride distilled off. The remaining anthracene was then analyzed. All runs were carried out in a thermostated bath at 25°.

It was assumed to be axiomatic that, irrespective of mechanism, the composition-time relation must be a first order law[11] of the form

$$\ln (F_0/F) = xt \qquad (1)$$

where F_0 and F are the fractional abundances of deuterium in anthracene initially and after a reaction time of t seconds, respectively. However, in all acid mixtures it was found that the value of x increased as the completion of the reaction is approached (Fig. 1). We attribute this to a secondary complication, probably the formation of small amounts of sulfonic acids, the presence of which would increase the solubility of anthracene in the acid phase (see Discussion). The initial slope of curves like that in Fig. 1 was therefore used for evaluating x. Equation 1 assumes that the loss of each of the two atoms of deuterium in molecules of 9,10-anthracene-D_2 in sample X proceeds at the same rate (which will occur if the atoms are equivalent and isotopic substitution at a 9-position does not significantly affect the rate of replacement at a 10-position as is certain). Equation 1 is directly applicable to runs followed by analysis method (a). Analysis method (d) was used in most of the kinetic experiments. In this procedure the abundance of 9-anthracene-D_1 (M) is followed and the rate equation has to be modified to allow for the conversion of 9,10-anthracene-D_2 (B) to M

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[7] J. Bigeleisen, M. Perlman and H. Prosser, not yet published.

[8] W. H. Beisler and L. W. Jones, *ibid.*, **44**, 2296 (1922).

[9] L. Friedman, unpublished.

[10] E. L. Martin, This Journal, **58**, 1438 (1936).

[11] H. McKay, *Nature*, **142**, 997 (1938).

$$\ln\left[\frac{[\mathrm{M}]}{[\mathrm{M}]_0} - \frac{2[\mathrm{B}]_0}{[\mathrm{M}]_0}\left(e^{-xt} - e^{-2xt}\right)\right] = -xt \quad (2)$$

x was evaluated by successive approximations. The second term in the square brackets is small and can therefore be neglected for the first approximation. Refinement beyond a second approximation was not experimentally significant.

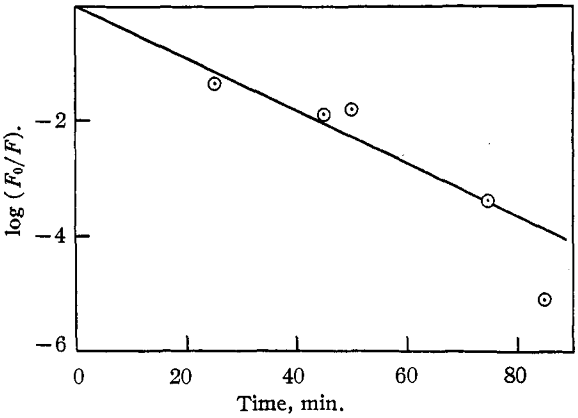

Fig. 1.—Kinetics of deuterium loss in 85.9% sulfuric acid.

No significant dependence of the reaction velocity on the stirring speed was observed at the stirring speeds employed. The dependence of the rate on the volumes of the phases was examined by observing the amount of exchange, using the same acid and time of reaction, for a range of volumes (25–75 ml.) of each of the two phases. A fairly good proportionality between x and V/V' was found to exist and an attempted correlation between x and $1/V'$ was clearly incorrect (V = volume of H_2SO_4 layer, V' = volume of CCl_4 layer).

As shown in Fig. 2, there is a fair linear correlation of log x and the acidity function, H_0, of slope −2.3 ± 0.2.

The Distribution of Anthracene between Sulfuric Acid and Carbon Tetrachloride.—Dilute solutions of anthracene (Eastman Kodak Co., Grade 480-X in 50 ml. of carbon tetrachloride) of known concentration were shaken with the sulfuric acid–water mixtures (25 ml.) employed in the exchange experiments. The layers were separated by centrifuging and the ultraviolet absorption spectrum of the sulfuric acid layer was measured by means of a Beckman DU spectrophotometer. For acids up to 90% H_2SO_4 the amount of anthracene extracted into the acid was a small fraction (up to a few per cent.) of the total. The absorption spectrum of the separated sulfuric acid layer varied with time owing · to interfering chemical reactions. Readings were therefore taken at timed intervals and initial extinction coefficients obtained by extrapolating a curve of a function of the extinction coefficient against time to the time of the separation of the layers.[6] Over the range 3–15 min. the initial extinction coefficient was independent of the time of shaking, and the equilibration therefore appears to be complete after 3 min. It also appears that during this time interval solubilization of anthracene in the sulfuric acid phase by sulfonic acids is unimportant. The intensity of the band at ~ 4200 Å. which is characteristic of solutions of anthracene in sulfuric acid[6] was taken to indicate the concentration in the sulfuric acid phase. The banded absorption spectrum typical of anthracene in inert solvents could not be detected even in the weakest acids.

The logarithm of the apparent distribution coefficient can be represented as an approximately linear function of H_0 of slope −3.3 ± 0.2 (Fig. 2), a result which may be interpreted along the lines previously suggested.[6]

Discussion

The kinetic analysis is based on the assumption that the exchange occurs as a homogeneous reaction in the acid phase. The neglect of reaction at the interface seems justified by the inappreciable effect of the stirring speed on the reaction velocity and by the observed dependence of the reaction velocity on the volumes of the phases. The exchange reaction in such a two-phase system may then quite generally be represented by

$$\text{RD in CCl}_4 \underset{-\mathrm{P}}{\overset{\mathrm{P}}{\rightleftarrows}} \text{RD in H}_2\text{SO}_4 \underset{-1}{\overset{1}{\rightleftarrows}}$$

$$\text{RDH}^+ \underset{-2}{\overset{2}{\rightleftarrows}} \text{RH in H}_2\text{SO}_4 \underset{\mathrm{P}}{\overset{-\mathrm{P}}{\rightleftarrows}} \text{RH in CCl}_4$$

although it is possible that no potential minimum corresponds to RDH^+, *i.e.*, that the steps 1 and 2 are synchronous and not independent of each other. In the case of anthracene the yellow color appearing on solution in sulfuric acid has been ascribed to a species of the structure (I) and RDH^+ in the above scheme for hydrogen isotope exchange at a *meso*-position of anthracene should therefore have distinct stability. The higher exchange rate at the *meso*-position relative to the other positions is consistent with this picture. Even for aromatic hydrocarbons of lower basicity than anthracene it has been shown[12] that certain electrophilic substitution reactions go through a cationic intermediate so that the steps corresponding to 1 and 2 above are kinetically distinct. In deriving the rate expression in terms of the rate constants of the separate steps, the assumption was made that the amounts of material stored at all intermediate stages are negligible compared with the initial and final stages and that the stationary state method may be applied. We may also neglect the storage of reagent in the form RH_2^+, and the step −2, since the reaction was carried out with a large excess of light sulfuric acid over anthracene-D_1. The velocities of the partitioning steps P and −P are

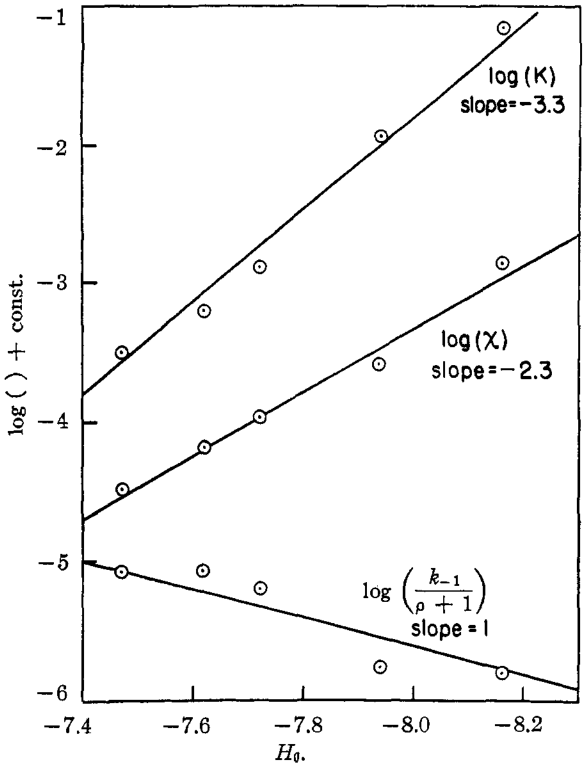

Fig. 2.—Dependence of K, x and (k_{-1}/ρ_{+1}) upon acidity.

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[12] L. Melander, *Arkiv för Kemi*, **2**, 211 (1950).

assumed to be unaffected by isotopic replacement and expressible in the form

$$\text{No. of moles crossing from phase A to phase B per sec.}$$
$$= k_{\mathrm{A}\rightarrow\mathrm{B}}C_{\mathrm{A}}\ (C_{\mathrm{A}},\ C_{\mathrm{B}} = \text{concn. in phase A,B})$$
$$= -V_{\mathrm{A}}\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = V_{\mathrm{B}}\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t}\ (V_{\mathrm{A}},\ V_{\mathrm{B}} = \text{volume of phase A,B})$$

where the constant $k_{\mathrm{A}\rightarrow\mathrm{B}}$ depends on the area and physical condition of the interface in the same way as the constant $k_{\mathrm{B}\rightarrow\mathrm{A}}$ corresponding to the reverse step. The individual reaction velocities in the sulfuric acid phase are written in the form $v = k \times$ concentration of organic species, and the specific reaction rates k are therefore functions of solvent properties, both of the type expressible as direct concentration effects and of that usually expressed as medium and salt effects.

Letting primed square brackets represent concentrations in the carbon tetrachloride phase and unprimed ones concentrations in the sulfuric acid phase and V' and V the corresponding volumes of the phases, the three stationary state conditions may be written

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{RD}] = \frac{k_{\mathrm{P}}}{V}[\mathrm{RD}]' + k_{-1}[\mathrm{RDH}^+] - \left(k_1 + \frac{k_{-\mathrm{P}}}{V}\right)[\mathrm{RD}] = 0$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{RDH}^+] = k_1[\mathrm{RD}] - (k_{-1} + k_2)[\mathrm{RDH}^+] = 0$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{RH}] = k_2[\mathrm{RDH}^+] + \frac{k_{\mathrm{P}}}{V}[\mathrm{RH}]' - \frac{k_{-\mathrm{P}}}{V}[\mathrm{RH}] = 0$$

Substitution of these conditions in the rate equations

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{RD}]' = \frac{k_{-\mathrm{P}}}{V'}[\mathrm{RD}] - \frac{k_{\mathrm{P}}}{V'}[\mathrm{RD}]'$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{RH}]' = \frac{k_{-\mathrm{P}}}{V'}[\mathrm{RH}] - \frac{k_{\mathrm{P}}}{V'}[\mathrm{RH}]'$$

and integrating between the limits 0 and t, leads to the expression

$$x \equiv \frac{1}{t}\ln\frac{F_0}{F} = \frac{1}{V'} \times \frac{k_{\mathrm{P}}k_1k_2}{k_1k_2 + \frac{k_{-\mathrm{P}}}{V}(k_{-1} + k_2)} \quad (3)$$

recalling that $F = [\mathrm{RD}]'/[\mathrm{RD}]' + [\mathrm{RH}]'$. This expression holds even if irreversible destruction of RD and RH occurs, *e.g.*, by sulfonation, *so long as* there is no isotope effect on the rate of this reaction. Since sulfonation does not normally attack the 9-position of anthracene this condition is almost certainly satisfied and the sulfonation will not upset the results by a fractionation effect of its own.

Since there exists an experimental proportionality between x and V/V' it follows that

$$\frac{k_{-\mathrm{P}}}{V}(k_{-1} + k_2) >> k_1k_2$$

i.e., the partitioning step is not completely or partially rate-controlling, and therefore

$$x = \frac{V}{V'} \times \frac{k_{\mathrm{P}}k_1}{k_{-\mathrm{P}}}\frac{k_2}{k_{-1} + k_2} \quad (4)$$

The equilibrium constant for the reaction

$$\mathrm{RH\ in\ CCl_4} \underset{-\mathrm{P\ (low\ concn.)}}{\overset{\mathrm{P}}{\rightleftharpoons}} \mathrm{RH\ in\ H_2SO_4} \underset{-1}{\overset{1}{\rightleftharpoons}} \mathrm{RH_2^+}$$

which is measured in the distribution study, if the identification of the yellow species with $\mathrm{RH_2^+}$ is correct, may be expressed in terms of some of the above rate constants, making the assumption that the rates of proton addition to RD and to RH are the same and the rates of proton loss from $\mathrm{RDH^+}$ and $\mathrm{RH_2^+}$ are identical, except for the statistical factor.

$$K = \frac{[\mathrm{RH_2^+}]}{[\mathrm{RH}]'} = \frac{k_{\mathrm{P}}2k_1}{k_{-\mathrm{P}}2k_{-1}} \quad (5)$$

The statistical factor of two appearing in the denominator and numerator happens to be the same. Combining equations 4 and 5 and writing $\rho = k_{-1}/k_2$ we obtain

$$x = \frac{V}{V'} \times K \times \frac{k_{-1}}{(\rho + 1)}$$

If we may assume that the value of K is the same at the concentration of the exchange experiments and at that of the distribution experiments, combination of the experimental results of Tables II and III leads to a set of values of $k_{-1}/\rho + 1$ at the different acid concentrations which is given in the last column of Table II. The ratio ρ is expected to be independent of medium composition and to have a value of ~ 7.[13-15]

TABLE II

DEPENDENCE OF EXCHANGE VELOCITY ON ACID CONCENTRATION

$V = 25$ ml., $V' = 50$ ml., [anthracene]$' = 0.05$ M

$\mathrm{H_2SO_4}$, % by wt.	10^4x, sec.$^{-1}$	$-H_0$	$k_{-1}/\rho + 1$, sec.$^{-1}$
84.0	5.2	7.47	3.3
85.0	10	7.62	3.4
85.9	17	7.72	2.5
87.8	43	7.94	0.7
90.0	230	8.16	0.6

TABLE III

DISTRIBUTION OF ANTHRACENE BETWEEN AQUEOUS SULFURIC ACID AND CARBON TETRACHLORIDE

$\mathrm{H_2SO_4}$. % by wt.	Concn. in $\mathrm{CCl_4}$	$\frac{\text{Concn. in H}_2\text{SO}_4}{\text{Concn. in CCl}_4}$	$-H_0$
84.0	2.3×10^{-2}	0.0003_2	7.47
85.0	2.3×10^{-2}	$.0006_2$	7.62
85.9	4.6×10^{-3}	.0014	7.72
87.8	2.3×10^{-3}	.012	7.94
90.0	2.2×10^{-4}	$.07_3$	8.16

The large value of k_{-1} accounts for the immeasurably fast rate of attainment of equilibrium in the distribution experiments. The integrated rate equation for this may be given in the form[16]

$$\mathcal{K} \equiv \frac{1}{t}\ln\frac{Q_\infty\left(1 + \frac{V}{V'}Q\right)}{Q_\infty - Q} = \frac{\frac{k_{-\mathrm{P}}k_{-1}}{V} + \frac{k_{\mathrm{P}}k_1}{V'}}{k_1 + \frac{k_{-\mathrm{P}}}{2V}}$$

where $Q = [\mathrm{RH_2^+}]/[\mathrm{RH}]'$ which becomes $\mathcal{K} = 2\ k_{-1}$, if it is assumed that $k_{-\mathrm{P}}k_{-1}/V >> k_{\mathrm{P}}k_1/V'$ and $k_{-\mathrm{P}}/2V >> k_1$. The step -1 is a proton abstraction reaction and the rate constant k_{-1} should therefore be a sum

$$k_{-1} = \Sigma(k^{\mathrm{B}}_{-1}[\mathrm{B}])$$

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(13) O. Reitz, *Z. physik. Chem.*, **A179**, 119 (1937); **A184**, 429 (1939).

(14) F. H. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949).

(15) V. J. Shiner, *ibid.*, **74**, 5285 (1952).

(16) We are indebted to Mr. D. P. N. Satchell for checking the algebra of this and the previous derivation.

the terms of which correspond to proton abstraction by the various basic species present in the solvent. In principle, each of the k^{B}_1 is still a function of the properties of the solvent and may therefore vary with the concentration of sulfuric acid. However, the kinetic analysis of a number of nitration reactions in sulfuric acid[17] has shown that this medium effect on rate constants can be relatively unimportant. The falling off of the rate constant k_{-1} with increasing acidity is therefore likely to be attributable to the changing concentration of the possibly active proton abstracting bases H_2O, $SO_4^=$ and HSO_4^- but the present data are insufficient to carry the analysis further. Experiments to extend these data with other compounds are in progress. Since

$$\log x = -2.3H_0 + \text{constant} \qquad (6)$$

and

$$\log K = -3.3H_0 + \text{constant} \qquad (7)$$

it follows that, very approximately

$$\log k_{-1} = H_0 + \text{constant} \qquad (8)$$

although the accumulation of experimental errors in the value of k_{-1} does not allow a sensitive test of this equation. From the definition of Hammett's acidity function we obtain that

$$\log \frac{k_1}{k_{-1}} = \log \frac{[RH_2^+]}{[RH]} = pK_{RH_2^+} - H_0 \qquad (9)$$

It follows from a combination of equations 8 and 9 that the rate of proton attachment to anthracene is rather insensitive to the medium composition over the particular range studied, which would be expected if the logarithms of the concentrations of the kinetically active acids in the solvent (probably H_2SO_4 and/or H_3O^+) change less rapidly than those of the kinetically active bases. The steep dependence of the rate constant x on the acidity is therefore almost entirely ascribed to the effect of acid concentration on the solubility of anthracene molecules in the sulfuric acid phase and hence on the ratio k_P/k_{-P}.

ITHACA, NEW YORK

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(17) A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3318 (1950); T. G. Bonner, F. Bowyer and G. Williams, *ibid.*, 3274 (1952).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Titanomagnetite and Ferric Titanate

BY S. S. TODD AND E. G. KING

RECEIVED MAY 20, 1953

Heat capacity measurements of titanomagnetite (Fe_2TiO_4) and ferric titanate (Fe_2TiO_5) were conducted throughout the temperature range from 51 to 298.16°K. Titanomagnetite has two heat capacity peaks, at 56.0 and 99.1°K. The entropies at 298.16°K. are, respectively, 39.0 ± 0.6 and 37.4 ± 0.3 cal./deg. mole for titanomagnetite and ferric titanate.

Introduction

Two compounds are known in the $FeO-TiO_2$ system,[1] ilmenite ($FeTiO_3$) and titanomagnetite (Fe_2TiO_4). In the $Fe_2O_3-TiO_2$ system, only one ferric titanate compound (Fe_2TiO_5) is definitely known. Compounds of composition corresponding to arizonite ($Fe_2O_3:3TiO_2$) and natural pseudobrookite ($2Fe_2O_3:3TiO_2$) sometimes have been postulated, but Overholt, Vaux and Rodda[2] have demonstrated by X-ray diffraction studies that arizonite is a mixture, and Pauling[3] similarly has demonstrated this for natural pseudobrookite.

Shomate[4] has reported low-temperature heat capacity values and the entropy at 298.16°K. for ilmenite, but there are no previous similar data for titanomagnetite or ferric titanate, with which the present paper is concerned.

Materials.—The compounds used in this investigation were prepared by K. R. Bonnickson of this Laboratory. The titanomagnetite was made from titania (99.8% pure), and powdered iron and magnetite derived from reagent grade ferric oxide. These ingredients were mixed in proper proportions and heated in a stream of nitrogen for several periods (including a total of 24 hours at 1250–1350° and 4 hours at 1350°), with intervening grindings, mixings, analyses and adjustments of composition. The final product analyzed 64.28% ferrous oxide and 35.66% titania, as compared with the theoretical 64.27 and 35.63%. Silica amounting to 0.06% was present. The X-ray diffraction pattern was virtually identical with that of magnetite, the only difference being a minor displacement of lines, corresponding to the slightly altered lattice dimensions.

The ferric titanate was made from pure titania and reagent-grade ferric oxide. An intimate, stoichiometric mixture was heated for several periods (including a total of 24 hours at 1200° and 7 hours at 1450°), with intervening grindings, mixings, analyses and adjustments of composition. Final analysis gave 66.63% ferric oxide and 33.30% titania, as compared with the theoretical 66.65 and 33.35%. The principal impurity was 0.06% silica. The X-ray diffraction pattern agreed with that for ferric titanate (Fe_2TiO_5) given in the A.S.T.M. catalog.

Measurements and Results

The heat capacity measurements were conducted with previously described apparatus.[5] The sample masses were 371.71 g. of titanomagnetite and 247.31 g. of ferric titanate. The results, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, are listed in Table I and plotted in Fig. 1. Molecular weights accord with the 1951 International Atomic Weights.[6]

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