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Competitive Electrophilic Protodedeuteration of the Monodeuterotoluene Isomers: the +I Effect[1]

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A brief study of the acid-catalyzed hydrogen–deuterium exchange reactions of toluene has shown the *ortho* position to be 1.09 ± 0.04 times as reactive as the *para* position toward aqueous perchloric acid, while the *meta vs. para* reactivity ratio was only 0.065 ± 0.012. This appears to be the first unambiguous example of +I inductive activation of the *ortho* position in aromatic electrophilic substitution.[11] Rather surprisingly, when the attacking agent was the bulky molecular acid, $C_3F_7CO_2H$, the *ortho/para* reactivity ratio was decreased by a factor of 2.5. This unexpectedly large effect is attributed to increased steric requirements of the attacking reagent in the latter case.

In the electrophilic replacement reactions of mono substituted benzenes the *ortho/para* ratio of attack is determined by polar as well as by steric influences.[3] Steric factors specifically deactivate the *ortho* position relative to unsubstituted benzene,[4] while polar effects may either activate or deactivate, and may operate with reasonable selectivity at either the *para* or the *ortho* position. Few chemists today question the validity of the concept of inductive activation, known as the "+I effect."[3] Curiously, and possibly as a result of this widespread acceptance, the +I effect has not received unambiguous experimental confirmation. No examples of the electrophilic replacement of aromatic hydrogen have been reported in which the *ortho* position is activated relative to both the *meta* and the *para* positions, although such activation is required for proof of the existence of inductive activation toward electrophilic reagents.[3]

In connection with other isotopic orientation studies soon to be submitted for publication,[1] a reliable infrared method of analysis for the isomeric monodeuterotoluenes had been developed.[5,6] It was then possible to carry out brief studies of the competitive electrophilic protodedeuteration[7] of the monodeuterotoluene isomers. Parallel experiments were run with strong aqueous perchloric acid and with anhydrous heptafluorobutyric acid in order to demonstrate the dependence of orientation on the nature of the attacking reagent.

Results and Discussion

The reaction conditions used and the infrared analytical results obtained are presented in Table I. Runs 1, 2 and 3 were performed to establish approximate relative reactivities for the ring positions in toluene. At the high level of deuterium content employed in these runs significant amounts of di- and polydeuterated toluenes were formed by reverse exchange. The infrared spectra of these species are not known, but almost certainly do not closely resemble those of the corresponding monodeuterotoluenes in the spectral regions used for analysis.[5,6] It follows that an observed decrease in the concentration of, for example, *o*-deuterotoluene must to some extent represent formation of species such as *o,p*-dideuterotoluene, and must therefore not be a true measure of the reactivity of the *ortho* position.

Fortunately it proved possible to carry out equally precise infrared analyses for the monodeuterotoluene isomers in dilute solution (3.22 mole %) in toluene. In the competitive protodedeuterations carried out at this thirty-fold dilution, the formation of dideuterated toluenes was wholly negligible, and the relative rates of disappearance of the isomeric monodeuterotoluenes accurately represented the relative reactivities of the ring positions toward the acids chosen. The reversibility of the exchange reaction made necessary the somewhat elaborate kinetic analysis described in the Experimental section. This treatment has been applied to the experimental data to give the results listed in Table II.

The first point of interest concerns the exchange reaction between toluene and 70.8% aqueous perchloric acid. Although two phases are present, it is likely that exchange takes place in the acid phase.[8,9] The possibility that diffusion between the phases might be significantly rate-controlling is unlikely here[10] but might well be quite important under conditions such that ten- or hundred-fold faster homogeneous exchange rates were observed. Studies at higher temperatures therefore were not carried out.

The *ortho* position of toluene was found to be 1.09 ± 0.04 times as reactive as the *para* position toward aqueous perchloric acid while the observed *meta/para* reactivity was only 0.065 ± 0.012. The latter ratio may be taken as confirmation that the protodedeuteration reaction is authentically elec-

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[1] Presented at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 11, 1955, Abstracts, p. 7-O.

[2] Charles A. Coffin Fellow, 1950–1951; Central Research Dept., Minnesota Mining and Mfg. Co., St. Paul, Minn.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 221–305.

[4] Unless steric strain is relieved in the activated complex; *cf.* R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **76**, 6353 (1954).

[5] G. V. D. Tiers, *J. Chem. Phys.*, **19**, 1072 (1951).

[6] G. V. D. Tiers and J. H. Tiers, *ibid.*, **20**, 761 (1952).

[7] J. F. Bunnett, *Chem. Eng. News*, **30**, 4019 (1954); *J. Chem. Soc.*, 4715 (1954); J. F. Bunnett, M. Morath and S. Okamoto, THIS JOURNAL, **77**, 5055 (1955). This simple and systematic scheme of nomenclature for substitution reactions has proved particularly useful for the case of hydrogen–deuterium exchange.

[8] V. Gold and F. A. Long, *ibid.*, **75**, 4548 (1953).

[9] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 3609, 3619, 3622 (1955).

[10] G. T. Barry, Y. Sato and L. C. Craig, *J. Biol. Chem.*, **174**, 209 (1948), report the results of rate studies on the exchange of solutes between phases. The half-life for phase exchange, expressed in units of "number of inversions," varies from one to, in a few cases, ten inversions. For the perchloric acid experiments we report here the half-life for phase exchange should lie between 0.5 and 5 seconds. The apparent deuterium exchange half-life was 21 hours, but, upon correcting for the limited solubility of toluene in perchloric acid, the true homogeneous half-life for *para*-protodedeuteration is only 19 seconds. Nevertheless, it seems probable that phase exchange is not of limiting importance in these experiments.

Table I

Competitive Electrophilic Protodedeuteration of Monodeuterotoluene Isomers by Aqueous Perchloric Acid and by Anhydrous Heptafluorobutyric Acid

Run	Temp., °C.	Time, hr.	Acid, g.	Toluene mixture, g.	Initial concn. of isomers of C_7H_7D, %[a] o	m	p	Final concn. of isomers of C_7H_7D, %[a] o[b]	m[b]	p[b]
($HClO_4$ aq.)										
1	22	300.0	1.67	0.873	0.0	0.0	100	13.1	9.0	6.3
2	22	12.75	1.67	.873	0.0	50.0	50.0	0.0	48.9	40.3
3	22	12.75	1.67	.873	50.0	0.0	50.0	40.8	0.5	39.9
4	27	37.0	1.67	.862	0.00	1.61	1.61	0.17	1.52	0.53
5	27	21.5	1.67	.862	1.61	0.00	1.61	0.92	0.02	0.88
($C_3F_7CO_2H$)										
6	78	88.0	2.63	0.172	0.00	0.00	0.00	0.00	0.00	0.00
7	78	70.0	2.79	.172	0.00	1.61	1.61	..	1.59	1.24
8	78	112.5	2.63	.172	0.00	1.61	1.61	0.03	1.53	1.12
9	78	70.0	2.79	.172	1.61	0.00	1.61	1.54	0.03	1.27
10	78	112.5	2.63	.172	1.61	0.00	1.61	1.38	0.01	1.10
11	119	7.0	5.75	.215	0.00	0.00	0.00	0.00	0.00	0.00
12	119	7.5	5.75	.215	0.00	1.61	1.61	0.05	1.56	0.92
13	119	20.3	5.75	.215	0.00	1.61	1.61	0.13	1.51	0.35
14	119	10.7	5.75	.215	1.61	0.00	1.61	1.15	0.00	0.73
15	119	24.7	5.75	.215	1.61	0.00	1.61	0.90	0.03	0.31

[a] Concentrations refer to the toluene mixtures added and recovered, and are expressed in units of mole percentage. [b] The analytical precision is ±0.6 in runs 1–3 and is ±0.016 in all other runs.

Table II

Calculation of Relative Reactivities and Pseudo First-order Rate Constants for Protodedeuteration of the Monodeuterotoluenes by $HClO_4$ and by $C_3F_7CO_2H$

Run	F	Calcd. concn. of isomers of C_7H_7D,[a] % (from back-reaction) o	m	p	Final concn. minus calcd. concn. of isomers of C_7H_7D,[a] % o	m	p	Protodedeuteration rate const. ratios k_0/k_p	k_m/k_p	Max. error	Protodedeut. rate const.[b] (p-position) $10^6 k_p$, sec.$^{-1}$
($HClO_4$ aq., two phase reaction)											
4	0.830	0.189	0.016	0.090	(−0.02)	1.50	0.44		0.065	±0.012	9.7 ± 0.3[c]
5	.626	.167	.001	.077	0.75	(+0.01)	0.80	1.09		± .04	9.1 ± .3[c]
($C_3F_7CO_2H$, homogeneous reaction)											
7	.31	.007	.001	.008	(.....)	1.59	1.23		0.06	± .04	1.08 ± 0.05
8	.45	.020	.002	.020	(+0.01)	1.53	1.10		0.13	± .05	0.94 ± .04
9	.19	.007	.000	.008	1.53	(+0.03)	1.26	0.21		± .15	0.97 ± .05
10	.34	.028	.003	.028	1.36	(+0.01)	1.08	0.43		± .04	0.99 ± .04
12	.50	.017	.002	.017	(+0.03)	1.56	0.90		0.05	± .02	21.6 ± 1.0
13	.89	.089	.012	.071	(+0.04)	1.49	0.28		0.045	± .007	23.9 ± 0.8
14	.53	.051	.006	.049	1.10	(−0.01)	0.67	0.44		± .04	22.8 ± 0.6
15	.78	.146	.020	.114	0.74	(+0.01)	0.20	0.37		± .06	23.4 ± 1.0

[a] Concentrations refer to the recovered toluene mixtures, and are expressed in units of mole percentage. The analytical precision is ±0.016 for the concentrations obtained by difference. [b] Average values of the pseudo first-order rate constant for p-protodedeuteration (expressed as $10^6 k_p$ in sec.$^{-1}$) are: for runs 4 and 5, 9.4 ± 0.3; for runs 7–10, 0.99 ± 0.04; for runs 12–15, 22.9 ± 0.7. The mean deviations are not larger than experimental error. [c] If correction is made for the solubility of toluene in the perchloric acid, 0.21 g./l., the average value of k_p for runs 4 and 5 becomes 38600 ± 1200 × 10^6 sec.$^{-1}$.

trophilic. The greater-than-unity *ortho/para* reactivity ratio found here is believed to be the first unambiguous example of +I inductive activation in electrophilic aromatic substitution.[11]

In the perchloric acid experiments it is reasonable to suppose that the attacking reagent is the hydrated proton, H_3O^+, and that exchange takes place by way of intermediate formation of a "σ-complex" carbonium ion[8,12] as originally proposed by W. G. Brown.[13] It was therefore of particular interest to extend the study to include protodedeuteration by a strong, non-aqueous molecular acid of relatively low dielectric constant. Such acids are trifluoroacetic acid and presumably also heptafluorobutyric acid.[14] The latter was chosen in these studies for its higher reflux temperature and

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[11] A Referee has suggested that the observed greater reactivity of the *ortho* position may be due instead to hyperconjugation. A molecular-orbital treatment by V. A. Crawford, *J. Chem. Soc.*, 2058 (1953), indicated such a charge distribution in the isolated toluene molecule, but by the reasoning of G. S. Hammond, This Journal, **77**, 334 (1955), the molecular orbital treatment of G. W. Wheland, *ibid.*, **64**, 900 (1942), is more likely to be applicable. In both cases it is the inductive effect of the methyl group that produces the predicted differences between *ortho* and *para* positions and, as Crawford has pointed out, it is difficult to demonstrate the specific effects of hyperconjugation in the presence of inductive effects.

[12] H. C. Brown and J. D. Brady, This Journal, **74**, 3570 (1952)

[13] W. G. Brown, A. H. Widiger and N. J. Letang, *ibid.*, **61**, 2597 (1939).

[14] W. Dannhauser and R. H. Cole, *ibid.*, **74**, 6105 (1952), have shown the dielectric constant of CF_3CO_2H to be 8.42 at 20° and 7.83 at 50°. From the low specific conductivity found for anhydrous CF_3CO_2H (3 to 5 × 10^{-7} mho/cm. at 25°), about ten times that for anhydrous acetic acid, the autoprotolysis constants for these acids must be of similar order of magnitude. The considerable strength of trifluoroacetic acid is indicated by Hammett acidity function studies reported in the Experimental section.

for the higher solubility of toluene in it. Homogeneous reactions at two temperatures were desired to bring out any extreme changes in orientation. The results of these experiments are presented in Tables I and II.

Toward anhydrous heptafluorobutyric acid the *ortho* position of toluene was only 0.4 times as reactive as the *para* position. The *meta/para* reactivity ratio, approximately the same as that found for aqueous perchloric acid, confirms the electrophilic nature of the reaction and indicates that the "substitution activity"[15] is about the same for the two reagents.

A question arises as to why the *ortho* position of toluene is relatively less reactive toward heptafluorobutyric acid than it is toward aqueous perchloric acid. Such a pronounced change in reactivity would not seem consistent with Gold's claim that exchange proceeds by way of a π-complex proton-bearing aromatic ion.[9] It is possible that the relative stabilities of the isomeric σ-complexes (and therefore of the activated complexes) might be so altered by the great change in dielectric constant as to bring about the observed change in orientation on passing from perchloric to heptafluorobutyric acid.[11] If this factor were operative the *ortho/para* ratio would be temperature-dependent; the limits of experimental error could not be made sufficiently narrow to exclude this possibility. An alternative explanation, more consistent with current orientation theory,[3] would attribute the difference to the temperature-independent steric requirements of the proton donor. Were this verified, then to accept Gold's view of the importance of the π-complex[9] it would become necessary to make *ad hoc* assumptions concerning steric effects upon its rearrangement to the σ-complex.

In this connection it might be expected that the nature of the "activated complex" would differ in the two media. The free π-complex proton-bearing aromatic ionic reactant,[9] the charge-bearing activated complex, and the free σ-complex carbonium ion intermediate favored for aqueous media are very much less likely in heptafluorobutyric acid; instead, exchange may occur by way of a non-ionized bridged complex.[16]

There is no reason to suppose that steric effects have been eliminated in the exchange with perchloric acid; a larger *ortho/para* ratio might be expected if, for example, anhydrous hydrogen fluoride were used.

Experimental

Materials.—The ring-monodeuterated toluenes used in this work have been described elsewhere.[6] The perchloric acid was reagent grade; its concentration was 70.8% by weight as determined by density measurement.[17] The heptafluorobutyric acid[18] was redistilled before use. Small amounts of volatile material and of high-boiling residue were thereby removed. The boiling point observed, 120° (750 mm.), agreed well with the reported value, 120° (735 mm.).[18] Water, if present, would have been removed as the azeotrope of b.p. 99°; no indication of such a fraction was found, but the first distillate of $C_3F_7CO_2H$ was nevertheless discarded. The presence of trace quantities of water cannot be excluded.

Perchloric Acid Experiments. Runs 1–3.—One ml. each of monodeuterotoluene mixture and of 70.8% aqueous perchloric acid were pipetted into a standard "one-half dram" glass vial, which was fitted with a Teflon-lined screw cap. The reactions were run at room temperature, 22 ± 2°. Thorough mixing of the two phases was provided by means of inversion of the vial by rotation once to twice per second throughout the reaction period.

Reactions were stopped by separation of the toluene phase. The toluene was dried and purified by a bulb-to-bulb distillation through P_2O_5 in a vacuum system.

Infrared analysis, performed upon 3.22 volume % solutions of the recovered toluene in tetrachloroethylene, made use of the 15 to 17 μ region characteristic for aryl deuterium.[6] Apart from possible interference by polydeuterated species, the analytical error is considered to be ±0.6 in each mole percentage. The analytical results thus obtained are presented in Table I.

Runs 4 and 5.—In order to eliminate interference resulting from polydeuteration the initial deuterotoluene mixtures (as used in runs 2 and 3) were diluted with pure ordinary toluene.[19] The total mole percentage of C_7H_7D was 3.22% in each case. The protodedeuteration runs 4 and 5, listed in Table I, were carried out at 27 ± 2° by the technique already described.

Infrared analyses were done directly on these dilute solutions in toluene as recovered from the reaction mixtures. It was essential to use the intense infrared bands characteristic of aryl deuterium in the 15 to 17 μ region[6]; deuterium-free toluene is almost transparent in this region and it does not interfere. High precision was attained through direct spectrophotometric measurement of percentage transmission by a cell-in-cell-out technique combined with a rigorous averaging procedure in which as many as twenty separate transmission measurements were made on each peak. Although Beer's law certainly was obeyed to a first approximation, a second-order departure was observed which was attributable to the need for use of a spectral band width appreciably greater than the actual absorption peak width. Therefore the conventional plot of concentration *vs.* optical density was not used. Instead, the calibration data, obtained by analysis of a number of varied synthetic test mixtures, was plotted in the form of concentration/optical density *vs.* optical density, and the best straight lines were drawn through the points. If the analytical error is considered to be equivalent to ±0.016 in each calibration percentage, all calibration points fell on these lines.

Heptafluorobutyric Acid Experiments. Runs 6–10.—The reaction mixtures, made up according to the proportions given in Table I, were homogeneous and did not require shaking; glass vials were used as previously, and reactions were run at 78.0 ± 0.5° in a thermostated oil-bath. Reactions were terminated by pouring the mixtures into excess sodium hydroxide solution. A very narrow-necked flask was used for these neutralizations in order that the toluene phase might readily be collected by flotation, without undue handling losses. The samples were dried and analyzed as described for the perchloric acid runs 4 and 5. Results are presented in Tables I and II.

Runs 11–15.—These reactions were conducted at reflux temperature, 119 ± 1°, in a 5-ml. flask with integral condenser, protected by a drying tube. Workup and analysis were as given previously.

Solubility of Toluene in Perchloric Acid.—Comparison of the spectrum of a saturated solution of toluene in 70.8% perchloric acid with that of an equal thickness of a 0.2142 gram per liter solution in heptane[20] showed close correspondence in wave lengths, band widths and intensities.

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(15) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953); H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300, 2306, 2310 (1955).

(16) C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1637 (1936).

(17) G. F. Smith and O. E. Goehler, *Ind. Eng. Chem.*, **3**, 61 (1931).

(18) A generous sample of heptafluorobutyric acid was kindly provided by the Minnesota Mining and Mfg. Co., St. Paul, Minn. The properties are given in the technical data sheet, "Heptafluorobutyric Acid," Minn. Mining and Mfg. Co., 1949, and were subsequently published by R. N. Haszeldine, *J. Chem. Soc.*, 2789 (1950).

(19) Toluene, Eastman Kodak Co., No. 325-X (regenerated from the sulfonic acid) had $n^{20}{}_D$ 1.4969, $d^{25}{}_4$ 0.86216 ± 0.00003, f.p. −94.7 ± 1.0°. F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," Nat. Bur. Stds. Circular C-461, Washington, D. C., 1948, p. 43, lists for toluene $n^{20}{}_D$ 1.4969, $d^{25}{}_4$ 0.86230, f.p. −94.991°.

(20) "Catalog of Ultraviolet Spectra," Am. Petr. Inst. Research Project 44, Carnegie Inst. of Tech., Pittsburgh, Pa., Serial No. 12.

Thus, the concentration of toluene in saturated solution in perchloric acid is approximately 0.21 gram per liter at 25°.

Estimate of the Hammett Acidity Function of Fluorinated Acids.—The Hammett acidity function, H_0, for 70.8% perchloric acid is approximately −7.0.[21] The fluorinated acids were much weaker; for anhydrous trifluoroacetic acid there was found $H_0 = -4.4 \pm 0.3$, and for anhydrous heptafluorobutyric acid, $H_0 = -3.3 \pm 0.3$. Benzalacetophenone was used as indicator at a concentration of 0.100 mg./ml. To eliminate solvent effects, integrated intensity measurements were made on the band at 4200 Å., after subtracting the background absorption due to the intense peak at 3245 Å.

Kinetics of Competitive Protodedeuteration.—The mathematical analysis of protodedeuteration is based on the customary assumption of first-order kinetics.[22] For the two-phase toluene–perchloric acid system it is further assumed that the rate of mixing is sufficiently great as to introduce no serious complications.[8,10] The desired rate constant ratios were obtained essentially by Ingold's competition method.[23,24] In its original form this method requires irreversible reactions, whereas the exchange reactions are obviously reversible. The usual analysis, applicable to simple exchange reactions,[25] cannot be applied directly, as four deuterated species and five independent rate ratios are involved. Fortunately, three of these may be chosen as the ratios of forward to reverse exchange rate constants for the three deuterotoluenes, and as such may be equated to the deuterium equilibrium separation factor, K, for the system. In the present work this was not measured, but for aromatic positions *vs.* strong aqueous acid, and at low deuterium concentrations such as were employed here, reasonable numerical values fall in the region $K = 1.00$ to 1.15. This constant is defined as[26]

$$K = \frac{\%\text{ D per (reactive) position, } C_7H_8}{\%\text{ D, } HClO_4\text{ aq. (or } C_3F_7CO_2H)}$$

For 70.8% perchloric acid we adopt the low value, $K = 1.00$, as it leads to the minimal value for the ratio k_o/k_p, and thus is least favorable to our interpretation; however, use of $K = 1.20$ results in a ratio larger by only 0.02. In the case of anhydrous heptafluorobutyric acid the choice is less critical: the value $K = 1.00$ is adopted for convenience.

The modification which permits use of Ingold's competition method is most simply described as follows. Protodedeuteration may be treated as an irreversible reaction which proceeds to completion if the mathematical fiction of distinguishing the particular deuterated molecules initially present from those formed (and destroyed) during the reaction is adopted. This procedure is rigorous, provided that the amounts of each deuterotoluene isomer formed *during* the reaction (and therefore not present initially) can be computed accurately; these amounts are then subtracted from the total amounts of each deuterotoluene found by infrared analysis at the completion of the reaction. The differences thus obtained represent the remaining amounts of the "initially present" deuterated molecules. These amounts decrease irreversibly to zero according to first-order kinetics and may be treated by Ingold's method.

The justification for this approach rests on the fact that the re-introduction of deuterium obeys a mathematically complex growth law as a result of the increasing deuterium content of the reacting acid. This increase is itself not linear and is dependent on the values of the two remaining independent rate ratios.

Attempts to obtain explicit solutions of the differential equations were abandoned and attention was turned to iteration processes. First, it was assumed that the increase in concentration of deuterium in the reacting acid could be represented to good approximation as first order. The corresponding rate constant, k_A, necessarily must be related to the concentrations of the initially-present deuterotoluene isomers and to their rate constants for protodedeuteration. Thus in the case of mixtures of *m*- and *p*-deuterotoluene we used $k_A = k_p$, while for the half-and-half mixtures of *o*- and *p*-deuterotoluene we adopted $k_A = (k_o + k_p)/2$. The low reactivity of the *meta* position was neglected.

For the perchloric acid phase the limiting deuterium concentration (in excess of the natural abundance of deuterium) in these experiments is calculated as 0.280% if all ring positions of toluene are equilibrated. If, however, the *meta* positions of toluene are considered unreactive and contain no deuterium the calculated metastable equilibrium percentage is 0.312%, and if half of the C_7H_7D were the *meta* isomer the metastable equilibrium percentage calculated for the acid phase becomes 0.156%. The effect of the observed slight reactivity of the *meta* position in toluene is taken into account in each case by increasing (or decreasing) these quantities proportionately to the amount of deuterium lost (or gained) at the *meta* position, as determined by analysis of the reaction product. Thus, for runs 4 and 5 (Tables I and II), the (metastable) equilibrium concentrations of deuterium in the perchloric acid phase are taken as 0.165 and 0.309%, respectively.

In the heptafluorobutyric acid experiments the (metastable) equilibrium deuterium concentration for the acid, calculated in exactly similar fashion, is 0.162% for run 7, 0.168% for run 8, 0.324% for run 9, 0.338% for run 10, 0.111% for runs 12 and 13, and 0.220% for runs 14 and 15.

Although it is not exact, when taken together with the choices of values for k_A given above this method of correction is found to result in negligible error.

With the help of these assumptions and approximations a differential equation was written which related the rate of formation of any monodeuterotoluene isomer (by the "reverse reaction," namely, deuterodeprotonation of the toluene solvent) to the rate of increase of the deuterium concentration in the acid phase. This differential equation was integrated[27] and was subjected to the pertinent boundary conditions; the time variable then was eliminated by appropriate substitutions of the equations defining the rate constants. The resulting equations, given below, were in a form suitable for application to the experimental data.

$$G = F + (1 - F)\ln(1 - F) \qquad (R = 1) \qquad (1)$$

$$G = [1 - RF - (1 - F)^R]/1 - R \qquad (R \neq 1) \qquad (2)$$

Here G is that fraction of the (metastable) equilibrium concentration of the deuterotoluene isomer in question which is formed by virtue of "parasitic" deuterodeprotonation during the competitive protodedeuteration experiment. It is expressed as a function of F, the fraction of the (metastable) equilibrium deuterium concentration attained by the acid during the experiment, and of R, the rate constant ratio, k/k_A for deuterium exchange at the ring position under consideration.

For the reactions in question the deuterium content of the acid is of necessity the amount not accounted for in the toluene. The numerical values of F are listed in Table II. The constant, k_A, has been specified already in terms of the protodedeuteration rate constants.

The desired rate constant ratios, k_o/k_p and k_m/k_p, are found by a process of iteration (successive approximation). Starting with any approximate values for these ratios, *e.g.*, (for perchloric acid) $k_o/k_p = 1$, $k_m/k_p = 0.05$, first approximations are obtained to R, and thence to G, for each deuterotoluene isomer in each run, by way of equations 1 and 2. Plots of F *vs.* G and of G *vs.* R are convenient for this purpose. First approximations to the amount of each isomer formed by "parasitic" deuterodeprotonation in each run are obtained by multiplying each of these G values by the calculated (metastable) equilibrium acid-phase deuterium concentration (as given above) and by the appropriate statistical factor (*o*- and *m*-C_7H_7D, 2; *p*-C_7H_5D, 1). These

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[21] L. P. Hammett and M. Paul, THIS JOURNAL, **56**, 827 (1934); see also N. C. Deno and R. W. Taft, Jr., *ibid.*, **76**, 244 (1954).

[22] T. H. Norris, *J. Phys. Colloid Chem.*, **54**, 777 (1950); G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).

[23] C. K. Ingold, A. Lapworth, E. Rothstein and D. Ward, *J. Chem. Soc.*, 1959 (1931); C. K. Ingold and M. Smith, *ibid.*, 905 (1938).

[24] T. S. Lee, in "Technique of Organic Chemistry," A. Weissberger, ed., Vol. 8, Interscience Publishers, Inc., New York, N. Y., 1953, pp. 100–130.

[25] P. R. O'Connor, ref. 24, pp. 80–99.

[26] J. A. Dixon and R. W. Schiessler, THIS JOURNAL, **76**, 2197 (1954), reported $K = 1.12 \pm 0.05$ for the distribution of deuterium between benzene and 85% H_2SO_4. In a private communication Prof. Dixon has assured us that this value pertains to the constant as defined above, rather than to the reciprocal of this as erroneously stated in their article. It is thus in agreement with data reported by Ingold, *et al.*, *J. Chem. Soc.*, 1637 (1936). A similar but slightly lower value for K would be expected for 70.8% $HClO_4$.

[27] A. Cohen, "Differential Equations," D. C. Heath and Co., New York, N. Y., 2nd Ed., 1933, p. 30.

amounts are subtracted from the total amount of each isomer found by infrared analysis; the differences are treated by the method of Ingold to give first approximations to the desired rate constant ratios. The process is repeated until sufficiently exact values have been obtained for these ratios. The final values are listed in Table II.

The data provide two independent tests of the accuracy of this treatment. One of these concerns the nearness to zero of the parenthetical values in cols. 6 and 7 of Table II. These isomers were absent initially, and thus owe their presence completely to the "parasitic" deuteroprotonation reaction. The mean of the parenthetical values is +0.012, and the mean deviation is ±0.014. In view of the analytical precision, ±0.016, these values do not appear to be significantly larger than zero. The other, less sensitive, check of the treatment has to do with the good consistency of the pseudo first-order rate constants for *para*-protodedeuteration listed in the last column of Table II. These constants were obtained from the "corrected" concentrations shown in column 8 of Table II. If the method of correction were inappropriate, such consistency would hardly be expected.

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CHICAGO 37, ILL.

COMMUNICATIONS TO THE EDITOR

GASEOUS OXIDES OF ALUMINUM, TUNGSTEN, AND TANTALUM[1]

Sir:

Brewer and Searcy[2] have concluded that $Al_2O_3(l)$ vaporizes from a tungsten effusion cell at 2300–2600°K. according to the equation

$$Al_2O_3(l) \longrightarrow 2AlO(g) + O(g) \qquad (1)$$

They deduced that a reaction of the type

$$Al_2O_3(l) + ((3 - 2x)/y)W(s) \longrightarrow 2AlO_x(g) + ((3 - 2x)/y)WO_y(g) \qquad (2)$$

does not occur by a comparison of the weight of effusate collected with a chemical analysis for aluminum contained therein. They inferred, since Al_2O_3 is more volatile in a tantalum than in a tungsten cell, that the former reduces Al_2O_3 to $Al_2O(g)$ whereas the latter does not. Confident that stable tungsten oxide molecules exist at these temperatures, the authors have investigated directly the weight ratio of Al_2O_3 to tungsten transported upon complete vaporization of the Al_2O_3.

The outgassed tungsten cell was mounted in an evacuated water-cooled fused silica condenser. No radiation shields were employed except annular shields directly on the top of the cell to control the temperature of the top relative to that of the bottom. Hence only an insignificant amount of the effusate experienced reflection.

In a preliminary experiment it was found by spectroscopic analysis that tungsten had been transported to the condenser but not to a target at about 450°. The weight of material on the target agreed approximately with that found by Brewer and Searcy. Subsequent experiments yielded a weight ratio of Al_2O_3 to tungsten transported of 1.17 ± 0.02 at 2587°K. No deposition occurred below the orifice plane. It was also observed that milligram quantities of tungsten were transported within the effusion cell from one region to another at a higher temperature. Since the vapor pressure of tungsten is negligible at these temperatures, one concludes that tungsten is transported out of the cell by a gaseous oxide which is sufficiently unstable to cause transportation of tungsten by dissociation within the effusion cell. Hence, some oxygen must effuse out of the cell and the experimental weight ratio of Al_2O_3 to tungsten must be greater than that which one calculates assuming $WO_y(g)$ to be undissociated. This fact definitely eliminates only the products $AlO(g) + WO_3(g)$. For the possible combinations, $Al_2O(g) + WO(g)$, $AlO(g) + WO(g)$, and $Al_2O(g) + WO_3(g)$ the weight ratios are 0.28, 0.55, and 0.83, respectively.

Langmuir[3] has shown indirectly that $WO_3(g)$ exists at high temperatures. However, more detailed experiments are needed to distinguish among the other possibilities. In spite of this, the fact remains that Al_2O_3 and tungsten do react at high temperatures and that the free energies measured by vaporization of Al_2O_3 in a tungsten crucible correspond more closely to reaction (2) rather than (1).

The reaction with tantalum is more easily understood. The authors find that Al_2O_3 appears to vaporize from a tantalum cell according to the reaction

$$Al_2O_3(s) + 3/x\ Ta(s) \xrightarrow{1700^\circ} 3/x\ TaO_x(s) + 2Al(g) + yTa(s) \xrightarrow{2250^\circ} (3/x + y)TaO(g) \qquad (3)$$

on the basis of the metallic aluminum deposited on the condenser and the weight ratio of Al_2O_3 to tantalum transported of 0.19.

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) L. Brewer and A. W. Searcy, THIS JOURNAL, **73**, 5308 (1951).

(3) I. Langmuir, *ibid.*, **35**, 105 (1913).