88 to 55% while carbon dioxide remains unchanged at 95%. Hydrogen peroxide, therefore, is not a likely intermediate in this reaction as the Glasstone–Hickling theory predicts. The data in Table I illustrate some other interesting features relative to the Kolbe reaction and are worthy of comment. It will be recalled that the stoichiometry involved in the calculation of current efficiency assumes that the transfer of two electrons gives rise theoretically to one molecule of ethane and two molecules of carbon dioxide in the case of acetate and one molecule of ethylene but only *one* molecule of carbon dioxide in the case of propionate. The correctness of the assumption is borne out by the results. It is noteworthy that efficiency for both ethane and carbon dioxide are higher in acetic acid than water. This is because oxygen formation is greater in water. On the other hand hydrocarbon efficiency is generally lower than carbon dioxide efficiency. This is pronounced with propionate at high frequencies. The reason must be further oxidation of the radical or the hydrocarbon to non-gaseous products. These considerations do not, however, affect the mechanistic arguments made earlier.

Acknowledgments.—The authors wish to thank Drs. F. H. Verhoek, Boris Musulin and S. E. Lippincott for their helpful advice during the course of this investigation. They also wish to thank the du Pont Company for the Teaching Fellowship granted to W.T.L., and Mr. Kiefer Newman for designing and building the square wave generator.

East Lansing, Michigan

[Contribution from the Department of Chemistry, the Rice Institute]

Isotope Effects in Carbonium Ion Reactions. II. The Decomposition of *p*-Toluenediazonium Ion[1]

By Edward S. Lewis, Jimmy L. Kinsey and Robert R. Johnson

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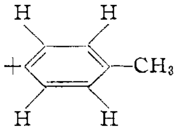
A precise method for the measurement of diazonium salt decompositions is described. The rate of decomposition of *p*-trideuteromethylbenzenediazonium ion in aqueous acid is shown to be about 1% faster than that of the undeuterated compound. The difference, which is significant, is understandable in terms of bond weakening by hyperconjugation and an aryl cation intermediate in diazonium salt decomposition.

Introduction

The substitution of deuterium for hydrogen in certain positions results in a retardation of the rate of some ionization reactions.[2] The explanation of this retardation involved weakening of the carbon–hydrogen bonds in the transition state by the contribution of unbonded structures, due either to solvent attack,[2a] or merely to hyperconjugation.[2b,c]

It is expected that such a rate retardation by deuterium substitution will be observed in general when the bond to the deuterium atom (and the corresponding hydrogen in the undeuterated compound) is weaker in the transition state than it is in the initial state of the reacting molecule. An obvious extension is that a molecule containing a stronger carbon–hydrogen bond in the transition state than in the initial state should react more rapidly on substitution of deuterium for the hydrogen. However, a faster reaction for a deuterium compound has not been observed before.

A reaction with more extensive hyperconjugation in the initial state than in the transition state is the decomposition of *p*-toluenediazonium ion in aqueous acid. In this molecule the *p*-methyl group produces a retardation not ascribable to an inductive effect, since the *meta*-methyl group accelerates.[3] The hyperconjugation in the diazonium salt is presumably more important than that in the resulting *para*-methylphenyl cation, accounting for the marked difference between the effects of *meta* and *para* alkyl substitution.[3b] In fact, the structures I and II do not combine for symmetry reasons, and the *para*-methyl group can stabilize the phenyl cation only by an inductive effect.[4]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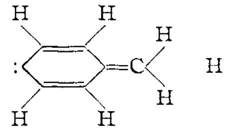
II

While the substitution of deuterium for hydrogen has influences other than that on the zero-point energy, it seemed, nevertheless, worthwhile to look at the sign and magnitude of the isotope effect in this reaction. Since only a very small effect can be expected, it was necessary to devise first a highly precise rate measurement usable with the small quantities of deuterated compound available.

Experimental

Materials.—*p*-Toluenediazonium fluoborate was made following the procedure of Lewis and Miller,[3b] but the yield is not great enough to make this preparation suitable for the deuterated compound. The starting point in the synthesis of the deuterated compound was *p*-acetaminotrideuterotoluene (III), the synthesis of which will be described in detail in a subsequent publication. In essence the route involved the high temperature hydrolysis and decarboxylation of the sodium salt of dimethylphenylmalonate with deuterium oxide. The resulting trideuterotoluene was acetylated, then converted to the acetaminotrideutero-

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[1] Presented before the Division of Physical and Inorganic Chemistry, at the spring meeting of the A.C.S., Dallas, 1956.

[2] (a) V. J. Shiner, Jr., This Journal, **75**, 5292 (1953); **76**, 1603 (1954); (b) C. E. Boozer and E. S. Lewis, *ibid.*, **74**, 6306 (1952); **76**, 794 (1954); **76**, 791 (1954); (c) E. S. Lewis and G. M. Coppinger, *ibid.*, **76**, 4495 (1954).

[3] (a) M. L. Crossley, R. H. Kienle and C. H. Benbrook, *ibid.*, **62**, 1400 (1940); (b) E. S. Lewis and E. B. Miller, *ibid.*, **75**, 429 (1953).

[4] We are indebted to Prof. M. G. Ettlinger for pointing out the orthogonality of the vacant orbital in I and the aromatic π-orbital.

toluene (III) by hydrazoic acid. The first steps of this synthesis are based on the method of Coppinger.[5]

The amide III (275 mg.) was boiled under reflux in a slow stream of nitrogen with 0.5 ml. of concd. hydrochloric acid, and three more 0.5-ml. portions of acid were added at intervals during the three hour hydrolysis. The resulting solution was evaporated to dryness with 0.8 ml. of 42% fluoboric acid, and the residue was mixed with 3 ml. of ether and 0.5 ml. of water and cooled in an ice and salt-bath. Ethyl nitrite (prepared on a small scale by the method of Semon and Demerell)[6] was passed into the mixture until a test with moist starch–iodide paper showed a persistent excess of the nitrite. The resulting suspension was filtered, yielding 205 mg. (57%) of the deuterated *p*-toluenediazonium fluoborate.

The deuterium content of the starting toluene was estimated by comparing the intensities of the aromatic and benzyl proton absorptions in a nuclear magnetic resonance spectrometer. This showed that all but about 13% of the hydrogen in the methyl group of toluene had been replaced by deuterium. This toluene had an ultraviolet spectrum essentially identical with that of undeuterated toluene, although many differences appeared in the infrared spectrum.

Rate Measurements.—The decomposition was followed by analyzing for unreacted diazonium salt, which was coupled with the salt of "R acid" (2-naphthol-3,6-disulfonic acid). The resulting azo compound was determined spectrophotometrically. A method of successive approximations to the rate constant eliminated many analytical errors. A rate constant was guessed, and then the times to take successive samples were calculated, such that the total quantity of diazonium salt in each sample would be the same. The successive sample sizes were ordinarily 10, 20, 50, 100 and 200 microliters, since accurate pipets of these sizes were available. The samples were collected at the calculated times, then added to an excess of the R salt (0.1 ml. of 0.02 *M* R salt in saturated sodium bicarbonate). After standing at room temperature for at least half an hour and then warming slightly (in case the coupling was not complete), the solutions were acidified with 1 ml. of 1 *M* hydrochloric acid, shaken to release the carbon dioxide and diluted to 10 ml. The optical densities were then measured at 498 mμ, the maximum, where the extinction coefficient was about 4×10^4. It can readily be shown that if the logarithm of optical density under these circumstances is plotted against time, the slope of the line is the correction to be applied to the initially guessed rate constant. The rapid convergence and insensitivity to analytical error of this method was shown by making a very bad initial guess of the rate constant for *p*-toluenediazonium ion, namely, zero, and a poor analytical method, namely, colorimetric determination of the azo compound in a visual colorimeter with a poorly matching color standard. At 52.8°, starting with the guess $k = 0$, the first corrected value obtained was $k = 3.5 \times 10^{-4}$ sec.$^{-1}$, and the next approximation was $k = 2.4 \times 10^{-4}$ sec.$^{-1}$, compared to the value 2.52×10^{-4} obtained in the more accurate analysis. Optical densities for the runs reported in the table were obtained using photoelectric spectrophotometers, and the results shown in the table are those of experiments where the correction term was less than 5%, although some preliminary experiments were run to obtain an initial assumed rate constant of the necessary accuracy.

A further reduction in error due to temperature fluctuations, pipet inaccuracy, clock errors, etc., was accomplished by putting two identical reaction vessels in adjacent positions in the thermostat, one containing the deuterium compound and one the ordinary one. Then the same pipets were used in the sampling for each compound, and the two rates were determined concurrently. The rate constants reported in the table were obtained from the slope of the best straight line calculated by the method of least squares to fit the logarithmic plot mentioned above. The fit was not perfect in all cases; but there did not appear to be any trend, and the inclusion or exclusion of the worst points did not have a marked effect on the calculated rate constants, and in particular did in no case alter the order of reactivity of the hydrogen and deuterium compounds. The tabulated rate constants are those based on all points.

TABLE I

RATES OF DECOMPOSITION OF *p*-TOLUENEDIAZONIUM ION

Temp., °C.	$k_H \times 10^4$	$k_D \times 10^4$	k_H/k_D[a]
35.9[b]	0.24_4	0.25_2	(0.97)
39.8	0.4065		
52.8	2.513	2.551	0.985
52.8	2.532	2.555	0.991
52.8[c]	2.567	2.581	0.995
52.8		2.560	0.988[d]
52.8	2.530		
52.8	2.483		
52.8	2.483		
62.2	8.51		

[a] Runs on the same horizontal line were concurrent. [b] At this low temperature a side reaction makes the rate constants rather less accurate. See text. [c] The high values for this pair of concurrent runs may have been due to a temperature drift in the thermostat. [d] Derived from the indicated pair of non-concurrent runs.

Discussion

The table indicates that the deuterium compound reacts perceptibly faster than the hydrogen compound, supporting the view that there is less hyperconjugation in the transition state than in the initial state. The significance of the results, however, depends entirely on the accuracy of the rate constants. The method used removes the burden of accuracy from the analytical method and has very non-exacting requirements for spectrophotometer linearity. Thus if the correction term on the guessed rate constant is about 5% of the rate constant, then the slope need only be determined to within 10% to give a final accuracy of 0.5%. The accuracy of the pipets and the dilution is in principle limiting with this method, and these are better than ±0.5%. We have made no attempt to reduce still further the errors in rate constant, since the temperature reproducibility from one run to the next probably is almost limiting already. The run marked *c* in the table may have been made at a perceptibly higher temperature. The temperature control in any one run or pair of concurrent runs is, however, not worse than 0.01°. The difference between the hydrogen and deuterium compound does not result from a difference due to a gradient in the thermostat, for the relative positions were not always the same.

A requirement for the successful application of this method is that the reaction be strictly first order and, furthermore, the product must not absorb significantly at the wave length used for the measurement. The run at 35.9° is not highly accurate because these requirements are not exactly met. At this low temperature (unlike the results at the higher temperature), the solution developed a color and the logarithmic plot was not quite linear. Presumably the diazonium salt couples slowly with the product, *p*-cresol. While this is not an important effect, the accuracy of the results is markedly reduced, and the figures given in the table are based on only the earliest points to reduce this effect.

An estimate of accuracy may be obtained by comparison with other data. The only work of comparable precision is that of Taylor and Feltis obtained with an elaborate gas evolution device.[7]

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(5) G. M. Coppinger, Thesis, the Rice Institute, 1953.

(6) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 204.

(7) J. E. Taylor and T. J. Feltis, THIS JOURNAL, **74**, 1331 (1952).

Figure 1 is an Arrhenius plot showing these data and ours. Our lowest temperature data are the least accurate; Taylor and Feltis claim least accuracy at their highest temperature. It is seen that the agreement is excellent in the region where high accuracy is claimed for both results. Better agreement would require better temperature measurements, since our temperatures are measured with a mercury thermometer calibrated by the National Bureau of Standards, with corrections listed to the nearest 0.1°. If we choose to ignore the advantage of the concurrency of the pairs of runs, we get the average $k_H = 2.518 \times 10^{-4}$ with a mean deviation of 0.025×10^{-4}; the average k_D then is 2.562×10^{-4} with a mean deviation of 0.019×10^{-4} and the ratio k_H/k_D is then 0.983. This includes all runs at 52.8°, including one made as much as a year before the final ones in a somewhat different thermostat (the last one in the table at this temperature). No reasonable selection of individual runs or combinations thereof will significantly change this ratio.

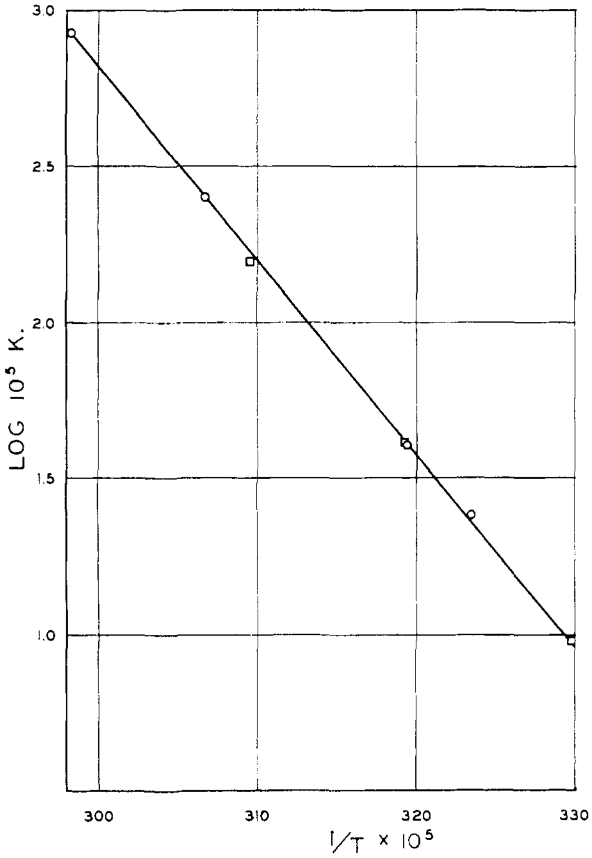

Fig. 1.—Arrhenius plot for the decomposition of *p*-toluenediazonium ion; data of Taylor and Feltis □; this work O.

While we cannot consider the ratio established to high accuracy the value 1.00 for the ratio is very improbable, being indicated in fact by only the one of the six values of k_H, the one which gave an unusually high value of k_D in the concurrent experiment. The value $k_H/k_D = 0.990 \pm 0.005$ covers the most reliable data combinations. The conclusions drawn at the beginning of this discussion are therefore justified, and both the connection between isotope effect and hyperconjugation and the suggested mechanism of diazonium salt decomposition can be considered to be confirmed by this unusual isotope effect.

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HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Products of the Thermal Decomposition of Bis-δ-phenylvaleryl Peroxide in Carbon Tetrachloride and in Benzene

BY DELOS F. DETAR AND CLAUS WEIS[1]

RECEIVED FEBRUARY 10, 1956

The thermal decomposition of bis-δ-phenylvaleryl peroxide has been studied in solution in carbon tetrachloride and in benzene. By use of dilute solutions (4–16 mmolar) and of an aliphatic type of peroxide, complicating induced decomposition reactions have been minimized. The expected δ-phenylbutyl radical intermediate is structurally capable of cyclizing to give tetralin; tetralin was formed in 30% yield in benzene but was absent from reactions in carbon tetrachloride. In carbon tetrachloride the products were CO_2 (84%), phenylvaleric acid, 4-phenyl-1-chlorobutane, δ-phenylbutyl δ-phenylvalerate, 1,8-diphenyloctane, 1,1,1,3-tetrachloro-5-phenylpentane (addition of CCl_4 to 4-phenyl-1-butene), hexachloroethane and phosgene. A careful search showed that the intramolecular chain transfer product, *o*-chloro-*n*-butylbenzene, was absent and also that 1,1,1-trichloro-5-phenylpentane was absent. This latter result is most significant, for it shows that there is no cross-coupling of 4-phenyl-1-butyl radicals with trichloromethyl radicals, although the products of separate coupling, hexachloroethane and 1,8-diphenyloctane, are formed. Such a result can be accounted for if the 1,8-diphenyloctane and the δ-phenylbutyl δ-phenylvalerate result form radical dimerization occurring in a solvent "cage" and if all 4-phenyl-1-butyl radicals which escape react to give 4-phenyl-1-chlorobutane. On this hypothesis more than 50% of the reaction in carbon tetrachloride occurs by primary or secondary recombination reactions.

The thermal decomposition of diacyl peroxides has been studied extensively by many investigators[2-5] because of the importance of this type of reaction as a source of free radical intermediates. In spite of the studies there remain a great many perplexing features about the mechanisms of the peroxide reactions. The difficulty stems from the fact that under most conditions a number of plausi-

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(1) Post-doctoral Research Associate. This work was supported by National Science Foundation Grant NSF G439.