

$\beta_{CO} = 0.8\beta_{CC}$ , and three different values for  $\beta_{CN}$ ;  $0.8\beta_{CC}$  (as in unhindered dimethylamino compounds),  $0.7\beta_{CC}$ , and  $0.5\beta_{CC}$ . Also reported are the energies of the h.f. m.o.'s of these compounds as determined from eq. 1 and from their polarographic oxidation potentials.

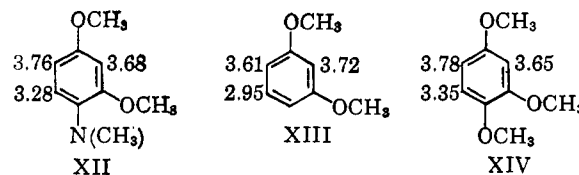
A 12.5% reduction of  $k\beta_{CN}$  (from  $0.8\beta_{CC}$  to  $0.7\beta_{CC}$ ) is found to give quite good agreement with the polarographic data. This reduction corresponds to an average out-of-plane angle of  $\sim 30^\circ$  for the sterically hindered dimethylamino group, assuming a cosine dependence of resonance integral on angle of interaction of atomic orbitals.<sup>24</sup>

To complete this examination of the choice of  $k_{CN}$  in hindered dimethylamino-substituted aromatics, a comparison of the aromatic proton chemical shifts and the calculated charge densities is indicated. Unfortunately, these are too few aromatic proton chemical shifts to use effectively a least-mean-squares treatment. All the aromatic protons of both X and XI were found to exhibit the same chemical shift ( $3.23 \tau$ ) under our standard conditions.

The average of the *calculated* charge densities (c.d.) at the ring positions contiguous to the ring proton positions in X and XI as a function of  $k_{CN}$  is:  $k_{CN} = 0.8$ , c.d. = 1.046;  $k_{CN} = 0.7$ , c.d. = 1.039;  $k_{CN} = 0.5$ , c.d. = 1.024. Using the relationship of chemical shift and charge density obtained for the sterically unhindered dimethylamines, with  $\alpha_N = \alpha_C + 1.0\beta_{CC}$ , a charge density of 1.022

is indicated for  $3.23 \tau$ . These data indicate that the hindered bond integral,  $k_{CN}$ , should be close to 0.5, although the limited number of experimental values does not permit too much significance to be attached to this figure.

We did not try to use XII in the n.m.r. correlation with charge density because the chemical shifts of other 1,2,4-trisubstituted benzenes had been irregular. The results for XII, however, throw some light on the situation. The diagram below shows what happens to the proton chemical shifts in 1,3-dimethoxybenzene<sup>5</sup> when



either a methoxy- or a dimethylamino group is added to the 4-position. The almost negligible differences in chemical shifts for the aromatic protons in XII and in XIV suggests that the alterations in the shifts in going from XIII are due at least in part to the restriction in rotation of the methoxy group in the 3-position. Further investigations of this effect are in progress.

**Acknowledgment.**—We wish to thank J. E. Lehnsen and S. M. Kern for their assistance in the molecular orbital computations.

[CONTRIBUTION OF THE CHEMISTRY DEPARTMENT, TEXAS CHRISTIAN UNIVERSITY, FORT WORTH, TEXAS]

## A Radiochemical Study of the Acetolysis of 3-Phenyl-2-butyl Tosylate

BY WILLIAM B. SMITH AND MAXINE SHOWALTER

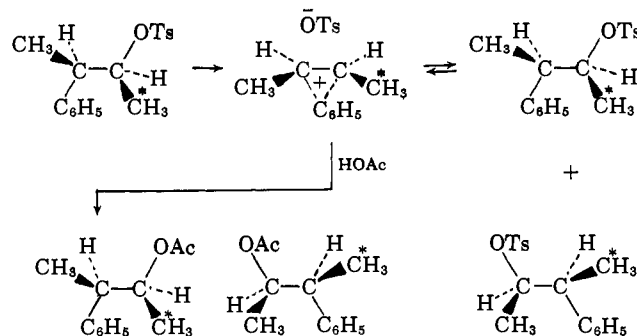
RECEIVED MAY 13, 1964

The acetolysis of (+)-*threo*-3-phenyl-2-butyl tosylate-1-C<sup>14</sup> at 75° produced racemic *threo*-3-phenyl-2-butyl acetate which, upon reduction and resolution, gave (+)-*threo*-3-phenyl-2-butanol showing no isotope position rearrangement and (–)-*threo*-3-phenyl-2-butanol with all of the label at C-4. These results are in accord with the postulated phenonium ion intermediate and provide a tool for measuring the ratio of internal return to product formation in the *erythro* system. By studying the rate of scrambling in recovered tosylate this ratio has been obtained for the acetolysis of both the *threo*- and *erythro*-tosylates. Data on the former system agreed reasonably well with the kinetic and polarimetric data in the literature. Comparisons between the two systems indicate that steric effects are of little importance in the rate of formation of phenonium ion–tosylate ion pairs in either system and may even slightly favor the *erythro* system, a result in conflict with the expected methyl eclipsing effects.

### Introduction

As the result of an extensive series of studies on the solvolysis and elimination reactions of the stereoisomers of 3-phenyl-2-butyl *p*-toluenesulfonate (tosylate) and related compounds, Cram and co-workers<sup>1</sup> postulated the formation of a symmetrically bridged phenonium ion–tosylate ion pair intermediate as a rationalization of the observed stereochemical consequences of the reaction. Support for the ion pair concept and a measure of the extent of internal return in the 3-phenyl-2-butyl tosylate system was provided by Winstein and Schreiber<sup>2</sup> who measured the polarimetric and titrimetric rates of solvolysis of (+)-*threo*-3-phenyl-2-butyl tosylate and who reported that for acetolysis the former exceeded the latter. Similar measurements on the

*erythro* system, of course, were not possible since collapse of the *erythro* ion pair to starting tosylate leads to material of retained configuration. The mechanistic scheme resulting from these studies may be summarized as



The postulation of the phenonium ion as an intermediate in the acetolysis of 3-phenyl-2-butyl tosylate

(1) (a) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); **71**, 3883 (1949); **74**, 2129 (1952); **74**, 2137 (1952); **74**, 2149 (1952); (b) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **75**, 3189 (1953); (c) D. J. Cram, H. L. Nyquist, and F. A. Abd Elhafez, *ibid.*, **79**, 2876 (1957).

(2) S. Winstein and K. Schreiber, *ibid.*, **74**, 2165 (1952).

imposes restrictions not only on the stereochemistry of the reaction but also on the fate of a radiocarbon label introduced at the C-1 position. For (+)-*threo*-tosylate, it is readily seen that the (+)-*threo*-acetate in the product must be formed with complete retention of the label at the C-1 position. The (–)-*threo*-acetate, on the other hand, should have all of the label rearranged to the C-4 position.

As will be shown, the expectations above have been verified in the acetolysis of (+)-*threo*-3-phenyl-2-butyl tosylate-1-C<sup>14</sup>. Having obtained this result, it then became possible to initiate a study of the rate of internal return and acetolysis in the *erythro*-3-phenyl-2-butyl tosylate system. Such data would be of considerable interest, making possible the evaluation of the role which such factors as the eclipsing effects of the methyl groups play in the ion-forming steps in both the *threo* and the *erythro* systems. The results of this study are also reported below.

### Experimental

The experiments described below with (+)-*threo*-3-phenyl-2-butyl tosylate were carried out several years ago. At the time, it seemed best to duplicate the original conditions used by Cram.<sup>1a</sup> In the subsequent kinetic study, the solvent and conditions were chosen so as to duplicate as near as possible those of Winstein and Schreiber.<sup>2</sup>

A sample of 3-phenyl-2-butanol-1-C<sup>14</sup> was generously supplied by Dr. C. J. Collins of Oak Ridge National Laboratory. The alcohol was separated into the *threo* and *erythro* racemates and the former resolved to obtain the (+)-*threo* isomer by the method of Cram.<sup>1</sup> The physical properties of the tosylates and their various derivatives agreed well with the data reported in the literature.

**The Acetolysis of (+)-*threo*-3-Phenyl-2-butyl *p*-Toluenesulfonate-1-C<sup>14</sup>.**—The acetolysis was run under the same conditions of time, temperature, and solvent as those reported by Cram.<sup>1</sup> The (+)-*threo*-tosylate ester (5.1 g.) was allowed to react for 35 hr. at 75.0° in 110 ml. of acetic acid solvent (14.1 g. of potassium carbonate, 25 ml. of acetic anhydride, and 1 l. of acetic acid). The rearranged product was recovered, reduced with lithium aluminum hydride, and chromatographed over alumina. The methanol eluent was distilled off leaving 1.02 g. of crude 3-phenyl-2-butanol. This material was converted to the acid phthalate derivative by treatment with an equal weight of phthalic anhydride in 4 ml. of pyridine at 100°. The product of the reaction was crystallized from ethyl acetate and petroleum ether to give 1.3 g. of racemic *threo*-3-phenyl-2-butyl acid phthalate, m.p. 127–128°,  $[\alpha]_D^{25} 0^\circ$  (*c* 3, 95% ethanol); reported<sup>1</sup> for the acid phthalate, m.p. 130–131°. Previous experience indicated that the low melting point was caused by the presence of a small amount of unreacted phthalic anhydride as an impurity.

In order to facilitate further handling of this material the radioactive acid phthalate (1.28 g.) was diluted with 1.10 g. of nonradioactive racemic *threo*-3-phenyl-2-butyl acid phthalate. The combined material was recrystallized from ethyl acetate and petroleum ether. As soon as a small amount of crystals had formed the solution was decanted and the crystallization then allowed to proceed. In this fashion 1.32 g. of pure racemic *threo*-3-phenyl-2-butyl acid phthalate, m.p. 130–131°, was obtained. The activity of this material was  $1.121 \pm 0.023$  mc./mole. Resolution through the brucine salt was carried out by the method of Cram<sup>1a</sup> to give 0.230 g. of pure (+)-*threo*-3-phenyl-2-butyl acid phthalate, m.p. 101–102°,  $[\alpha]_D^{25} +25^\circ$  (*c* 2.60, 95% ethanol); reported<sup>1</sup> for (+)-*threo*-3-phenyl-2-butyl acid phthalate, m.p. 101–102°,  $[\alpha]_D^{25} +25.2^\circ$ .

The (+)-*threo*-acid phthalate was hydrolyzed by heating in a sealed tube with 10 ml. of 15% potassium hydroxide for 17 hr. The tube was opened, and the contents were extracted with petroleum ether. Evaporation of the petroleum ether left an oily residue which was subjected to the iodoform reaction using the conditions developed by Bonner and Tanner.<sup>3</sup> The iodoform

was crystallized from methanol–water; m.p. 121–122°; activity,  $1.075 \pm 0.017$  mc./mole.

The material remaining from the above resolution was reconverted to the acid phthalate,  $[\alpha]_D^{25} -9.1^\circ$  (*c* 2.64, 95% ethanol), corresponding to 32% of the (+)-*threo* isomer and 68% of the (–)-*threo* isomer. A sample of this material was hydrolyzed and degraded in the fashion above. The radioactivity of the iodoform so produced was  $0.385 \pm 0.005$  mc./mole.

**Preliminary Kinetic Studies.**—As a check of the literature value of the acetolysis rates and as a preliminary technique check, three kinetic runs each were made on the acetolysis of *threo*- and *erythro*-3-phenyl-2-butyl tosylate. Solutions of the appropriate tosylate (0.03 *M*) were made up at room temperature in acetic acid solvent (containing 0.2% acetic anhydride). The sealed ampoule technique was used throughout. The rates were determined by titrating the amount of *p*-toluenesulfonic acid formed as a function of time using standard sodium acetate in acetic acid with brom phenol blue as an indicator. A standard least-squares treatment was used to determine the first-order rate constants. At 74.8°, the following experimental values with standard deviations were obtained: *threo*-3-phenyl-2-butyl tosylate,  $4.41 \pm 0.17 \times 10^{-5}$  sec.<sup>-1</sup>, and *erythro*-3-phenyl-2-butyl tosylate,  $5.12 \pm 0.21 \times 10^{-5}$  sec.<sup>-1</sup>; reported values<sup>2,4</sup> taken at 74.7 and 74.90°, *threo*-tosylate, 4.95 and  $5.15 \times 10^{-5}$  sec.<sup>-1</sup> and *erythro*-tosylate,  $5.77 \times 10^{-5}$  sec.<sup>-1</sup>. In view of the difficulties in repeating exact experimental conditions, we considered this as satisfactory agreement.

**Kinetic Studies with Labeled Tosylates.**—A typical run with labeled tosylate can be described as follows. A known volume of the acetic acid solvent (50.0 ml. measured at room temperature) was preheated to 74.8°, and 0.9277 g. of *threo*-3-phenyl-2-butyl tosylate-1-C<sup>14</sup> ( $4.381 \pm 0.005$  mc./mole) was added with swirling. The tosylate was allowed to react for the time calculated for 5% completion from the literature rate constant.<sup>1</sup> The reaction mixture was chilled in ice, allowed to come to room temperature, and two 1-ml. aliquots were withdrawn and titrated.

For recovery of the tosylate the reaction mixture was poured into an equal volume of water, then extracted with three portions of a 1:1 mixture of ethyl ether–petroleum ether. The solution was washed with water, dilute bicarbonate, water again, and then dried over anhydrous magnesium sulfate. The oil recovered after evaporation of the solvent was recrystallized several times from benzene–petroleum ether to give 0.68 g. of *threo*-tosylate, m.p. 47–48° ( $4.387 \pm 0.109$  mc./mole), reported<sup>1</sup> m.p. 46–47°.

The recovered tosylate was reduced to 3-phenyl-2-butanol by the procedure given below. This was degraded by the usual iodoform reaction, and the iodoform was assayed to give the percentage rearrangement in the recovered tosylate.

The titration data and the percentage rearrangement data for both the *threo*- and *erythro*-tosylates are given in Table I. These data were combined to calculate the equivalent to *k<sub>a</sub>* as determined by Winstein and Schreiber.<sup>2</sup> These values are also given in Table I. It should be pointed out that about 3 weeks work was required for each point.

**The Degradation of Recovered Tosylates.**—Tosylates recovered in the kinetic studies were reduced to the corresponding alcohols by means of sodium in liquid ammonia by the procedure of Denney and Goldstein.<sup>5</sup> A typical procedure for a sample of unrearranged *threo*-tosylate is described here.

To a solution of 0.24 g. (0.010 mole) of sodium in 50 ml. of anhydrous liquid ammonia was added a solution of 0.53 g. (0.0017 mole) of *threo*-tosylate in 25 ml. of anhydrous ether. The addition took place at the rate of about 4 drops per sec. Shortly after completion of the addition, the solution turned orange. The reaction mixture was stirred an additional 15 min.; sufficient solid ammonium chloride was then added to alter the color of the mixture to white. At this point, 5 ml. of water was added, and the ammonia was allowed to evaporate. The contents of the flask were extracted with four portions of ether which was dried over magnesium sulfate, filtered, and distilled away leaving 0.39 g. of yellow oil as a residue.

While the activity of the starting tosylate was  $4.381 \pm 0.005$  mc./mole, the iodoform<sup>3</sup> produced from the above oil assayed as  $4.035 \pm 0.035$  mc./mole, a 3.8% loss of activity. Purification of the iodoform by sublimation failed to improve the result.

(4) S. Winstein, B. K. Morse, E. Gruewald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

(5) D. B. Denney and B. Goldstein, *J. Org. Chem.*, **21**, 479 (1956).

(3) W. A. Bonner and D. D. Tanner, *J. Am. Chem. Soc.*, **80**, 1447 (1958).

TABLE I  
KINETIC DATA FOR THE ACETOLYSIS OF *threo*- AND  
*erythro*-3-PHENYL-2-BUTYL TOSYLATE-1-C<sup>14</sup> AT 74.8°

Run	Time, sec.	Per cent reacted	$k_t \times 10^5$ , sec. <sup>-1</sup>	Per cent rear-ranged	Per cent total involved	$k_\alpha \times 10^5$ , sec. <sup>-1</sup>
<i>threo</i> -Tosylate						
1	1020	4.31	4.32	22.57	26.88	30.73
		3.77	3.75	...	26.34	29.98
2	2130	9.84	4.84	36.04	45.88	28.76
		9.92	4.90	...	45.96	28.90
Av. value and std. dev.		4.4 ± 0.5		29.6 ± 0.9		
<i>erythro</i> -Tosylate						
1	889	4.59	5.29	14.00	18.59	23.14
		4.68	5.39	...	18.68	23.26
2	1824	9.25	5.32	24.48	33.73	22.56
		9.39	5.41	...	33.87	22.68
3	1824	8.86	5.09	22.27	31.13	20.45
		8.97	5.15	...	31.24	20.54
Av. value and std. dev.		5.3 ± 0.1		22.1 ± 1.3		

In subsequent reductions the crude alcohol product was diluted with a known weight of nonactive pure alcohol. The total was then converted to the phthalate ester which was recrystallized to constant radioactivity. Hydrolysis of the purified phthalate and degradation of the alcohol produced iodoform with the same assay as the phthalate ester. The yield of alcohol produced in the tosylate reduction step was calculated by the isotope dilution technique. Repeated yields of 41–42% were obtained.

### Results and Discussion

It is now well established both from this work and from the earlier studies of Cram<sup>1a</sup> that the acetolysis of (+)-*threo*-3-phenyl-2-butyl tosylate produces mainly racemic *threo*-3-phenyl-2-butyl acetate. As shown in the scheme presented earlier, the postulation of a phenonium ion intermediate in the reaction sequence imposes certain restrictions on the distribution of a radio-carbon label placed at the C-1 position of the starting tosylate. Reduction of the acetate products to racemic *threo*-3-phenyl-2-butanol followed by subsequent resolution to the (+)-*threo* and (-)-*threo* isomers should show all the label in the C-1 position in the (+)-isomer, while the (-)-isomer should have all of the label rearranged to the C-4 position. The results for (+)-*threo*-3-phenyl-2-butyl tosylate-1-C<sup>14</sup>, reported in the Experimental section, are completely in accord with this expectation and may be taken as additional support for the intermediacy of phenonium ions in this system confirming the optical activity results of Cram<sup>1a</sup> and the kinetic data of Winstein and Schreiber.<sup>2</sup>

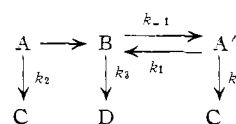
Having established this point, we now possessed a tool for examining in detail the role which internal return plays in the acetolysis of *erythro*-3-phenyl-2-butyl tosylate, for by recovering tosylate which had been subjected to acetolysis for known periods of time and by measuring the amount of radiocarbon scrambling, it should be possible to calculate the involvement of the tosylate in ion pair formation. Earlier studies of this sort had been carried out by Winstein and Schreiber in the *threo* system by measuring the polarimetric and titrimetric rates for the (+)-*threo*-tosylate.

In order to check the values of Winstein and Schreiber,<sup>2</sup> a preliminary study was carried out in which *threo*-3-phenyl-2-butyl tosylate-1-C<sup>14</sup> was allowed to undergo acetolysis for approximately 5 and 10% total

reaction. The recovered tosylates were then degraded and the percentage rearrangement of the carbon label determined. Coupled with titrimetric determinations of the amount of reaction in each case, one may then calculate the values of  $k_t$  and  $k_\alpha$  comparable to those reported by Winstein and Schreiber.<sup>2</sup> The values are given in Table I; the reported values<sup>2</sup> are  $k_t = 5.15 \times 10^{-5}$  and  $k_\alpha = 22.7 \times 10^{-5}$  sec.<sup>-1</sup>. We consider that the results reported in Table I are in satisfactory agreement with the literature values.

Subsequently a similar study was carried out using *erythro*-3-phenyl-2-butyl tosylate-1-C<sup>14</sup>. These results are also reported in Table I. The reported<sup>4</sup>  $k_t$  for the *erythro* system is  $5.77 \times 10^{-5}$  sec.<sup>-1</sup>. Again, our value for  $k_t$  is somewhat lower than the reported value. Since our studies in both systems were carried out in the same fashion, we have assumed that the results of these experiments are internally consistent. Comparisons of the two sets of titrimetric rate constants support this assumption. Values of  $k_\alpha$  in this study are no doubt less reliable than the value given for the *threo* system in the literature since we must use both the titrimetric data as well as the percentage rearrangement data in our calculations.

The detailed reaction scheme to be applied to these systems has been given by Cram and co-workers<sup>1</sup> and may be condensed as



where A is the appropriate optically active or radiocarbon labeled tosylate; A' is the racemic or rearranged tosylate formed after time  $t$ ; C and  $k_2$  represent the olefins and small amount of acetate formed by simple E1 or S<sub>N</sub>1 processes and the combined first-order rate processes leading to the formation of these products, respectively; and D is the acetate product formed directly from the intermediate ion pair.

The appropriate rate expressions have also been developed<sup>1,2</sup> and are

$$k_\alpha = k_1 + k_2 \quad (1)$$

$$k_t = k_2 + k_1 k_3 / (k_{-1} + k_3) \quad (2)$$

$$C/D = k_2 / [k_1 k_3 / (k_{-1} + k_3)] \quad (3)$$

Cram<sup>1b</sup> has determined the yields of products in the acetolysis of both the *threo*- and *erythro*-tosylates at 75° in the presence of a small amount of added sodium acetate. His results were: *threo*-tosylate, C 44% and D 56%; *erythro*-tosylate, C 27.4% and D 72.6%. In view of the observation that the presence of added sodium acetate exerts only a "normal" salt effect on the rates of reaction,<sup>2</sup> we assume that no alteration in the distribution of products will occur in the absence of the added salt and that the product analyses of Cram may be applied to our study. Using Cram's product data plus our data and the relations given above, the various rate constants in the scheme have been calculated. These figures are given in Table II.

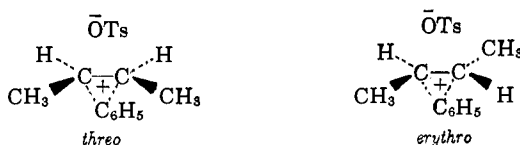
Two points of interest arise from a consideration of the values in Table II. The first has to do with the rather significant alteration of the ratio  $k_{-1}/k_3$  in going from the *threo*- to the *erythro*-tosylate. In certain de-

TABLE II  
RATE CONSTANTS FOR THE ACETOLYSIS OF *threo*- AND  
*erythro*-3-PHENYL-2-BUTYL TOSYLATE AT 74.8°

Tosylate	$k_{-1}/k_3$	$k_3/(k_{-1} + k_3)$	$k_1 \times 10^5$ , sec. <sup>-1</sup>	$k_2 \times 10^5$ , sec. <sup>-1</sup>
<i>threo</i>	10.3	0.09	27.4	2.2
<i>erythro</i>	4.4	0.19	20.7	1.4

tailed considerations of the mechanism of the solvolyses of the tosylates of 3-phenyl-2-butanol, 4-phenyl-3-hexanol, and 2,5-dimethyl-4-phenyl-2-hexanol, Cram, Nyquist, and Abd Elhafez<sup>1c</sup> made the then reasonable assumption that the ratio  $k_3/(k_{-1} + k_3)$  was the same in the respective *threo* and *erythro* systems. The results (Table II) obtained in this study are at variance with this assumption.

The geometric structures of the pertinent phenonium ion tosylate ion pairs may be represented as



Plainly eclipsing effects due to the methyls may be found in the *threo* but not in the *erythro* ion pair. Dissociation of the intimate ion pair into a solvent-separated ion pair or to a phenonium ion acetate ion pair should leave the geometry of the phenonium ion relatively unchanged and might be reasonably sup-

posed to proceed with about the same rate for either isomer. However, collapse back to the starting tosylate should be favored in the more highly strained *threo* ion pair. Thus, the ratios of  $k_{-1}/k_3$  can be rationalized with our determinations.

The second point arises from a consideration of the ratio  $k_1(\text{erythro})/k_1(\text{threo})$ . Based on the assumption of equal values of  $k_3/(k_{-1} + k_3)$ , Cram, Nyquist, and Abd Elhafez<sup>1c</sup> calculated the value of this ratio as 1.5 compared to our experimental value of 0.8. While the error in our experiments must be taken into account, it is evident that in actual fact the rate of phenonium ion formation for the *threo* isomer is at least as fast or perhaps even a little faster than the rate for the *erythro* isomer. This result implies that the energy differences between the ground state and transition state for the  $k_1$  process are very nearly alike. Clearly the differences imposed by eclipsing effects of the methyls are negligible in these systems.<sup>6</sup>

**Acknowledgment.**—The conception of this problem developed during the course of discussions held several years ago between Dr. D. J. Cram, Dr. C. J. Collins, and W. B. S. Grateful acknowledgment to these gentlemen for their help and encouragement is hereby extended. This work was supported by a grant from the Robert A. Welch Foundation whose aid is also gratefully acknowledged.

(6) For further inferences about eclipsing effects of methyls in related ionic reactions see W. B. Smith and W. H. Watson, *J. Am. Chem. Soc.*, **84**, 3174 (1962).

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

## The Electrochemical Oxidation of Acetic Acid in the Presence of Aromatic Hydrocarbons

BY SIDNEY D. ROSS, MANUEL FINKELSTEIN, AND RAYMOND C. PETERSEN

RECEIVED APRIL 24, 1964

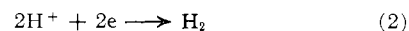
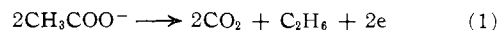
The electrochemical oxidation of acetic acid in the presence of benzene, ethylbenzene, *t*-butylbenzene, mesitylene, naphthalene, and phenyl acetate has been studied. Rates of gas evolution and the compositions of the gases produced have been determined. The major nongaseous products have been identified and determined. These products include both acetoxy and methyl derivatives with substitution occurring in both the ring and side chain. The many paths by which these products may have arisen are discussed, and particular attention is given to the possibility that many of the products arise from a prior discharge of the aromatic substrate at the anode to form a radical cation.

The electrochemical oxidation of carboxylate anions, described by Kolbe in 1849,<sup>1</sup> has been a subject of continuous investigation since that time.<sup>2</sup> Although still subject to controversy, the most widely accepted theory concerning the mechanism of this reaction is the discharged ion theory, proposed by Brown and Walker in 1891<sup>3</sup> and given experimental support by Clusius, *et al.*<sup>4</sup>

When 5 *N* aqueous acetic acid is electrolyzed under optimum conditions of high current density and high anodic potential, the anodic products are almost entirely carbon dioxide and ethane, formed in a mole ratio of 2 to 1 and with a current efficiency approaching 100%.<sup>5</sup> In less concentrated solutions or at lower

current densities or at lower anode potentials other anodic products—oxygen, methane, and methyl acetate—are also found.

In glacial acetic acid as solvent, the electrolysis of acetate ion is an even cleaner reaction, the over-all electrode reactions are almost exactly



and the coulombic yield approaches 2 moles of CO<sub>2</sub>, 1 mole of H<sub>2</sub>, and 1 mole of C<sub>2</sub>H<sub>6</sub> per 2 Faradays.<sup>6</sup> We find that when potassium acetate (5 g.) in glacial acetic acid (60 ml.) is electrolyzed at 20° at 0.4 amp. (1 cm.<sup>2</sup> platinum electrodes at a separation of 0.6 cm.), the rate of total gas production is 100 ± 1% of that demanded by the above equations, with the ratio CO<sub>2</sub>/

(1) H. Kolbe, *Ann. Chem.*, **69**, 257 (1849).

(2) For review articles see, B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952); "Advances in Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960, p. 1.

(3) A. Brown and J. Walker, *Ann. Chem.*, **261**, 107 (1891).

(4) P. Hölemann and K. Clusius, *Z. physik. Chem.*, **35B**, 261 (1937); K. Clusius and W. Schanzer, *ibid.*, **192A**, 273 (1943).

(5) K. Sugino, T. Sekine, and N. Sato, *Electrochem. Tech.*, **1**, 112 (1963).

(6) C. L. Wilson and W. T. Lippincott, *J. Am. Chem. Soc.*, **78**, 4290 (1956).