

calculations draw no distinction between chlorides of “ $\alpha$ -naphthyl” or “ $\beta$ -naphthyl” type.

Figures 7 and 8 show plots of  $\Delta E_{\pi}$  (fixed  $\beta$ ) vs.  $\log k$  for solvolysis of chlorides in 80% ethanol, and for their SN2 reactions with iodide ion in acetone, respectively. The points for the SN2 reaction lie fairly close to a straight line, with the exception of 9-chloromethylanthracene; the anomalously high reactivity of this could be a steric effect, it alone having no free position *ortho* to the chloromethyl group. The points in Figure 7 do not lie on a straight line, but a smooth curve can be drawn that passes close to them; Dewar

and Sampson<sup>24</sup> obtained similar curved plots for solvolysis of these chlorides in certain mixed solvents and pointed out that this could be explained very reasonably in terms of a change in structure of the transition state, this resembling a carbonium ion more closely in the case of the more reactive chlorides. As was pointed out in the sections on electrophilic substitution, the residual scatter in these plots may well be due to our failure to allow for variations in bond length; we hope soon to be able to modify our procedure so as to calculate the whole molecular geometry in a self-consistent manner.

## Kinetics of the Thallic Ion Oxidation of Olefins.

### II. Effect of Olefin Structure on Rate and Product Distribution

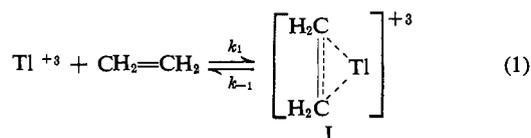
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The oxidation of ethylene, propylene, and the four butenes by aqueous thallic ion was found to give saturated carbonyl products and glycols as primary oxidation products. The reaction was first order in olefin and first order in thallic ion and not retarded by acid. The effect of structure on rate was analogous to that found for the hydration of olefins. Based on the kinetics and rate effects, a reaction scheme proceeding through an oxythallation adduct, in which the formation of the oxythallation adduct is rate determining, is proposed. The activated complex for oxythallation must have considerably more carbonium ion character than that for oxymercuration. The effect of olefin structure on product distribution is that expected if the products arise by decomposition of the oxythallation adducts postulated as intermediates, assuming thallium(I) behaves as a normal leaving group.

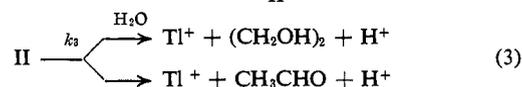
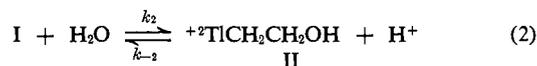
#### Introduction

Aqueous thallic ion oxidizes olefins to mixtures of glycols and carbonyl compounds.<sup>1</sup> In the first paper of this series,<sup>2</sup> the oxidation of ethylene to a mixture of acetaldehyde and ethylene glycol was found to be first order in thallic ion, first order in ethylene, not retarded by acid, and strongly accelerated by increasing salt concentration. On the basis of these results, plus supporting evidence, the following reaction scheme was proposed



(1) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).

(2) P. M. Henry, *J. Am. Chem. Soc.*, **87**, 990 (1965).



where  $k_1$  or  $k_2$  must be rate determining, since the reaction displays no proton inhibition. The effect of olefin structure on rates and distribution of products would depend greatly on the nature of the rate-determining step as well as the mode of decomposition of II. Therefore, to gain further insight into the mechanism of the reaction, the oxidation of propylene and the four butenes was studied.

#### Results

**Kinetics.** The reaction was studied in aqueous perchloric acid. All rates were measured by olefin uptake at olefin pressures of 1 atm. or less. During the course of a run, the olefin pressure was almost constant.

The rates of the oxidation of the substituted ethylenes were much faster than the rate for ethylene itself. To avoid mass transfer control of rate, the reaction was studied in a reactor of high gas-liquid mixing efficiency. Experimentally determined mass transfer coefficients were used to choose reaction conditions such that the rate constants measured were almost free of errors resulting from mass transfer control.

The reaction could be shown to be first order in thallic ion by plotting the data for a given run as described previously.<sup>2</sup> The reaction was found to be first order in olefin concentration for all olefins studied by measuring the pseudo-first-order rate constant at several different olefin pressures.

The values of the experimental second-order rate constants,  $k'$ , are listed in Table I for three different acid concentrations.

**Table I.** Values of the Second-Order Rate Constants at Three Acid Concentrations<sup>a</sup>

Olefin	HClO <sub>4</sub>			Rel. rate at 0.25 M HClO <sub>4</sub>
	0.1 M	0.25 M	0.5 M	
Ethylene	...	0.45 <sup>b</sup>	...	1
Propylene	65	75	88	167
1-Butene	63	73	106	162
<i>cis</i> -2-Butene	23	26	31	58
<i>trans</i> -2-Butene	5.5	6.1	6.6	13.6
Isobutene	... <sup>c</sup>	... <sup>c</sup>	... <sup>c</sup>	Ca. 2 × 10 <sup>8d</sup>

<sup>a</sup> Each value is an average of at least two runs. <sup>b</sup> Data from ref. 2. <sup>c</sup> Reaction too fast to be measured by methods used in this study. <sup>d</sup> Estimated by slowing the rate of oxidation by addition of acetate ion.<sup>3</sup>

As can be seen from Table I, the value of  $k'$  is not decreased by increasing acid concentration. The acceleration is no doubt of the same kind as observed previously with ethylene. The complete rate expression is thus

$$\frac{d[\text{TI}^{+3}]}{dt} = k'[\text{TI}^{+3}][\text{olefin}]$$

**Products.** The product distributions for the various olefins under conditions of low thallic ion and high mixing efficiency are given in Table II. At higher

**Table II.** Product Distribution for the Thallic Oxidation of Various Olefins<sup>a</sup>

Olefin	Carbonyl product	% carbonyl product	% glycol product <sup>b</sup>
Ethylene	Acetaldehyde	45 <sup>c</sup>	55 <sup>c</sup>
Propylene	Acetone <sup>d</sup>	75-85	15-25
1-Butene	Methyl ethyl ketone <sup>d</sup>	45-55	15-25
<i>cis</i> -2-Butene	Methyl ethyl ketone <sup>d</sup>	65-80	<0.5
<i>trans</i> -2-Butene	Methyl ethyl ketone <sup>d</sup>	65-80	<0.5
Isobutene	Isobutyraldehyde <sup>e</sup>	35-45	55-65

<sup>a</sup> Range given is the approximate range for several runs at different thallic ion concentrations. <sup>b</sup> Glycol product is always that expected from 1,2 addition to double bond. <sup>c</sup> Data from ref. 2. <sup>d</sup> No aldehyde product was detected by vapor phase chromatography (v.p.c.); limit of detection about 0.2%. <sup>e</sup> Traces of methyl ethyl ketone also detected by v.p.c.; yield was about 0.5%.

thallic ion concentrations or with poor mixing, secondary oxidation products such as acetol (from propylene) and 2-hydroxy-3-butanone (from 1-butene and *cis*- and *trans*-2-butene) were found. Control experiments showed that these products resulted from the further oxidation of the primary carbonyl products, rather than by further oxidation of the primary glycol products.

The total yields of primary oxidation products from ethylene, propylene, and isobutene usually accounted for over 90% of the thallic ion reduced. However, the total yields of products for 1-butene and *cis*- and *trans*-2-butene were never over 80% based on thallic ion reduced. Yields of methyl ethyl ketone as low as 65% were sometimes obtained with the 2-butenes. Other possible oxidation products, such as 1-buten-3-ol, crotyl alcohol, or crotonaldehyde were looked for but not found. The low yields probably result from the tendency of methyl ethyl ketone to undergo sec-

(3) P. M. Henry, unpublished data.

ondary oxidation. However, 2-hydroxy-3-butanone is not found under the conditions used to determine yields in this study. Possibly 2-hydroxy-3-butanone is rapidly oxidized further to other products such as diacetyl.

Isobutyraldehyde can, of course, arise from a pinacol rearrangement of isobutylene glycol. However, isobutyraldehyde must be a primary product, since the rearrangement is very slow under the conditions of the experiment (1 M HClO<sub>4</sub> at 25°).<sup>4</sup>

## Discussion

The two most likely mechanisms for this oxidation appear to be: (1) the one outlined in eq. 1 to 3; and (2) a mechanism involving positive oxygen transfer to form epoxides, followed by hydrolysis. The second can be rejected on the basis of the carbonyl products, since aldehydes rather than the ketones actually obtained would be formed where possible.<sup>5</sup> Also, the effect of structure on rate would be somewhat different from that found.<sup>5</sup>

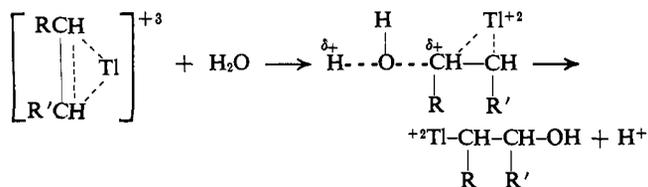
If the mechanism shown in eq. 1 to 3 is operable, then the decomposition of the oxythallation adduct (II), which determines the ratio of glycol to carbonyl products, cannot be the rate-determining step, since the lack of proton inhibition requires that the equilibrium represented by eq. 2 not be established. Thus, either  $k_1$  or  $k_2$  must be the slow step.

Since they are unrelated, the effects of structure on rate and distribution of products will be discussed separately.

**Effect of Structure on Rate.** Based on analogy with other metal ions, the rate variation with structure would support *neither*  $k_1$  *nor*  $k_2$  being rate determining. The tendency of Ag(I) to form  $\pi$ -complexes, as measured by the equilibrium constants, decreases with increasing substitution.<sup>6</sup> On the other hand, from the little evidence available, oxymercuration appears to be insensitive to olefin structure.<sup>3,7</sup> However, since  $\pi$ -complex formation with metal ions is a very fast reaction,<sup>8,9</sup>  $k_1$  seems very unlikely to be rate determining.

The effect of structure on rate in these reactions qualitatively parallels that found in the hydration of olefins.<sup>10-12</sup> If  $k_2$  is rate determining, the activated complex for oxythallation must have considerably more carbonium-ion character than that for oxymercuration. Thus, while oxymercuration is postulated to proceed by attack of water on a  $\pi$ -complex,<sup>13-15</sup> oxythallation proceeds by the rearrangement of a  $\pi$ -complex to an incipient carbonium ion which then reacts with water.

- (4) J. B. Ley and C. A. Vernon, *J. Chem. Soc.*, 2987 (1957).
- (5) S. Winstein and R. B. Henderson in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 1.
- (6) M. A. Muks and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).
- (7) E. R. Allen, J. Cartledge, M. M. Taylor, and C. F. H. Tipper, *J. Phys. Chem.*, **63**, 1442 (1959).
- (8) P. M. Henry, *J. Am. Chem. Soc.*, **86**, 3246 (1964).
- (9) P. Brandt, *Acta Chem. Scand.*, **13**, 1639 (1959).
- (10) L. L. Purlee and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **78**, 5811 (1956).
- (11) W. M. Schubert, B. Lamm, and J. R. Keefe, *ibid.*, **86**, 4728 (1964).
- (12) N. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965).
- (13) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).
- (14) P. Brandt and O. Plum, *Acta Chem. Scand.*, **7**, 97 (1953).
- (15) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963).



One possible consequence of the differences in mechanism could be a difference in stereochemistry between oxythallation and oxymercuration. Oxymercuration, as predicted from the postulated reaction scheme, is clearly *trans* for simple olefins but *cis* for bicyclic olefins such as norbornene.<sup>16,17</sup> Recently, oxythallation was shown to be *cis* to norbornene,<sup>18,19</sup> but, because of instability of the adducts, the stereochemistry of oxythallation of ordinary olefins has not been studied. The results of Anderson and Winstein<sup>20</sup> suggest that the oxythallation of cyclohexene in acetic acid may not be as clearly *trans* as oxymercuration.

Relative stabilities of the metal ion  $\pi$ -complexes, suggested as intermediates, may explain the differences between oxymercuration and oxythallation. The  $\pi$ -complex with Tl(III) might be expected to be weaker than that with Hg(II) because of the higher charge of the former ion. This higher charge reduces the size of the d orbitals to the extent that they are unable to give the d-p overlap which is postulated as necessary for strong  $\pi$ -bonding.<sup>21</sup> Thus, with Hg(II) the decomposition is by SN2 attack of water while with Tl(III) the  $\pi$ -complex decomposes by an SN1 route analogous to that for the hydration of olefins where the  $\pi$ -complex intermediate, if it indeed is an intermediate,<sup>11</sup> must be very weak.

*Effect of Structure on Product Distribution.* By analogy with oxymercuration, the structures of the oxythallation adducts would be those given in Table III.

**Table III.** Proposed Structure of Oxythallation Adducts

Olefin	Structure
Ethylene	$\text{HOCH}_2\text{CHTi}^{+2}$ (III)
Propylene	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Ti}^{+2}$ (IV)
1-Butene	$\text{C}_2\text{H}_5\text{CH}(\text{OH})\text{CH}_2\text{Ti}^{+2}$ (V)
<i>cis</i> - or <i>trans</i> -2-butene	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{Ti}^{+2}$ ( <i>threo</i> or <i>erythro</i> ) (VI)
$\text{CH}_3\text{CH}(\text{CH}_3)=\text{CH}_2$	$\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{CH}_2\text{Ti}^{+2}$ (VII)

Another reason for accepting these structures for propylene and 1-butene is that rationalizing the formation of ketones would be difficult if the hydroxyl were on the end carbon.

The most likely paths for decompositions of the oxythallation adducts are: (1) a hydride or methyl shift simultaneous with the thallium leaving with its electrons ( $\text{R} = \text{H}$  or  $\text{CH}_3$ ) to form a carbonyl compound (eq. 4), (2) attack of water on the carbon-thallium bond

(16) M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1961).

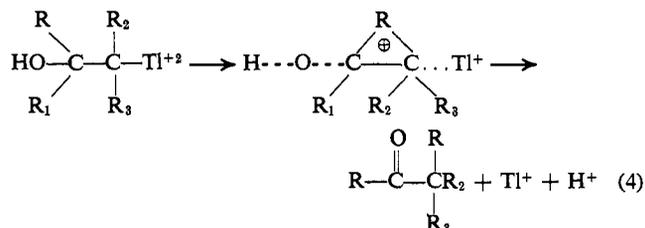
(17) T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, No. 19, 14 (1959).

(18) K. C. Pande and S. Winstein, *ibid.*, No. 46, 3393 (1964).

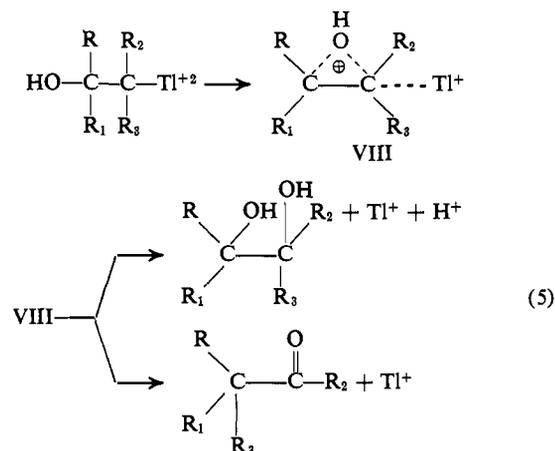
(19) F. A. L. Anet, *ibid.*, No. 46, 3399 (1964).

(20) C. B. Anderson and S. Winstein, *J. Org. Chem.*, 28, 605 (1963).

(21) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).



to give glycol, and (3) neighboring group participation by the hydroxyl group to give an intermediate resembling a protonated epoxide which would decompose to a mixture of carbonyl product and glycol.



Hydroxyl, a poor neighboring group,<sup>22</sup> would not be expected to decompose by route 3 unless the structure of the oxythallation adduct is extremely favorable for participation. Route 3 can be immediately eliminated for propylene and 1-butene; when the structure of VIII is such that  $\text{R}_2 = \text{R}_3 = \text{H}$  and  $\text{R}$  or  $\text{R}_1$  are alkyls (as for II and III), aldehydes, rather than the ketones actually found, would be expected.<sup>5</sup> The oxythallation adduct from ethylene (I) has a structure even less favorable<sup>23</sup> for participation than that of II or III, so its decomposition also must not follow route 3. The situation is less clear with *cis*- and *trans*-2-butene, since the test used above cannot be applied, but participation is unlikely since only ketone is found. The hydrolysis of the protonated epoxide (VIII) which would be obtained from VI would be expected to give high yields of glycol. Thus, the acid hydrolysis of *cis*- and *trans*-2,3-epoxybutane, which involves the same intermediate, gives almost quantitative yields of glycol.<sup>24</sup> The situation is reversed for isobutene. Decomposition of VII must involve hydroxyl participation, since isobutyraldehyde is formed.

Methyl or ethyl migration is not a factor in the decomposition of the oxythallation adducts from propylene, 1-butene, and *cis*- and *trans*-2-butene, since aldehydes are not detected as oxidation products. This is in keeping with the relative tendencies to methyl and hydride shift in alkyl carbonium ions.<sup>25</sup>

The ratio of carbonyl product to glycol is a measure of the relative amounts of hydride shift and hydrolysis of the carbon-thallium bond. With ethylene the ratio is about one, whereas for propylene and 1-butene the

(22) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, 70, 828 (1948).

(23) A. Streitwieser, Jr., *Chem. Rev.*, 56, 571 (1956).

(24) C. E. Wilson and H. J. Lucas, *J. Am. Chem. Soc.*, 58, 2396 (1936).

(25) L. C. Cannell and R. W. Taft, Jr., *ibid.*, 78, 5812 (1956).

hydride shift is favored by about four to one. This increase over that found for ethylene probably reflects the greater tendency to hydride shift for a hydrogen attached to a secondary carbon as compared with a hydrogen attached to a primary carbon.<sup>25</sup> Correcting for the statistical factor that III has two hydrogens available for hydride shift as compared with one for IV or V, the tendency to hydride shift in IV or V is about four times that for III. The large increase in hydride shift over hydrolysis in going to *cis*- and *trans*-2-butene is surprising but can probably be rationalized as the effect of steric hindrance to attack of water on a secondary carbon as opposed to attack on a primary carbon. It is unfortunate that no detectable amount of glycol was formed with either *cis*- or *trans*-2-butene, as the stereochemistry of the glycol would have defined the stereochemistry of the over-all reaction.

Perhaps the best way to test the mechanism involving an oxythallation intermediate is to compare the results in Table II with the results obtained for the solvolysis of structures analogous to those in Table III. Unfortunately, there are not many data available for comparison. The acid hydrolysis of 2-chloroethanol gives 1% acetaldehyde, and the remainder ethylene glycol.<sup>26</sup> The acid hydrolysis of 1-chloro-2-hydroxypropane in water gives a 42% yield of acetone and a 48% yield of 1,2-propylene glycol.<sup>27</sup> Thus, on the basis of these results, the larger carbonyl yield in the propylene oxidation over that found in the ethylene oxidation would be expected.

Although the product distribution obtained from *cis*- and *trans*-2-butene indicated the oxythallation adduct VI, obtained from these two olefins, did not decompose by hydroxyl participation, the solvolysis of a similar structure, 2-bromo-3-methoxybutane, in acetic acid and 80% dioxane, aided by silver acetate, does involve methoxyl group participation.<sup>28</sup> However, the change from methoxyl to hydroxyl, bromide to thallium(III), and the solvent from acetic acid or 80% dioxane to water could well change the mode of decomposition from one involving participation to one not involving participation.

On the other hand, the structure of the oxythallation adduct from isobutene is very favorable for participation.<sup>23</sup> The solvolysis of 2-methyl-1-methoxy-1-propyl *p*-bromobenzenesulfonate was found to proceed by neighboring hydroxyl participation, giving isobutyraldehyde as the main product.<sup>29</sup> Also the acid hydrolysis of 1-chloro-2-methyl-propan-2-ol apparently gives a mixture of isobutylene glycol and isobutyraldehyde,<sup>30</sup> indicating hydroxyl participation. The acid hydrolysis of isobutylene oxide<sup>31</sup> gives both isobutyraldehyde (5%) and isobutylene glycol (92%). Since the protonated epoxide intermediate in this reaction would resemble the intermediate VIII, for the decomposition of the oxythallation adduct from isobutene, the ratio of

(26) H. D. Cowan, C. L. McCabe, and J. C. Warner, *J. Am. Chem. Soc.*, **72**, 1194 (1950).

(27) I. K. Gregor, N. V. Riggs, and V. R. Stimson, *J. Chem. Soc.*, 76 (1956).

(28) S. Winstein and R. B. Henderson, *J. Am. Chem. Soc.*, **65**, 2196 (1943).

(29) S. Winstein, C. R. Lindgren, and L. L. Ingraham, *ibid.*, **75**, 155 (1953).

(30) G. J. Harvey, N. V. Riggs, and V. R. Stimson, *J. Chem. Soc.*, 3267 (1955).

(31) J. B. Ley and C. A. Vernon, *ibid.*, 3256 (1957).

carbonyl to glycol product might be expected to be very similar for the two reactions. The higher yields of isobutyraldehyde found in the decomposition of VII over those found for the hydrolysis of isobutylene oxide must mean the leaving thallium(I) exerts some influence on the decomposition of VIII. Perhaps it hinders the attack of water on VIII.

It is interesting to compare the decomposition of the oxythallation adducts with the solvolysis of mercury alkyls.<sup>32</sup> Here the solvolysis is postulated to be S<sub>N</sub>1 from the effect of structure of the alkyl group on rate. The S<sub>N</sub>1 mechanism for decomposition of the oxythallation adducts has not been considered, since the carbonium ion would collapse to VIII (eq. 5) and this would amount to neighboring group participation. These apparent differences between thallium(III) and mercury(II) are surprising, since they are isoelectronic and thallium(III) is the more vigorous oxidizing agent. Perhaps the difference lies in the solvation of the thallium(I) leaving group as opposed to mercury(0), the former requiring more solvent participation than the latter.

## Experimental Section

**Reagents.** The preparation and analysis of thallic ion stock solutions has been described.<sup>2</sup> The gases were Phillips Petroleum Company's either pure or polymerization grade. The results obtained were independent of the grade used. All other chemicals were of reagent grade.

**Identification of Products.** Acetone was identified by polarography, by vapor phase chromatography (v.p.c.), and by its semicarbazone and 2,4-dinitrophenylhydrazones derivatives. A reaction mixture in which all the thallic ion had been reduced by propylene was distilled and the semicarbazone derivative prepared from the distillate, m.p. 186.0–186.3° (lit.<sup>33</sup> m.p. 187°).

The 2,4-dinitrophenylhydrazones derivative, also prepared from the distillate of a reaction mixture, melted at 124.0–124.2° (lit.<sup>33</sup> m.p. 126°), m.m.p. with authentic derivative (125.0–125.1°) 124.9–125.0°.

Methyl ethyl ketone was identified by polarography, by v.p.c., and by its 2,4-dinitrophenylhydrazones and semicarbazones derivatives. The former derivative was prepared by direct treatment of a reaction mixture in which the thallic ion had been completely reduced with the reagent, whereas the semicarbazone derivative was prepared as described for acetone.

The 2,4-dinitrophenylhydrazones and semicarbazones derivatives of the butene oxidation products are listed in Table IV.

Isobutyraldehyde was identified by v.p.c., polarography, and by its 2,4-dinitrophenylhydrazones derivative, which was prepared from the distillate of the reaction mixture in which the thallic ion had been reduced by isobutene, m.p. 182.5–182.6° (lit.<sup>33</sup> m.p. 182°), m.m.p. with authentic derivative (182.5–182.8°) 181.0–181.3°.

Acetol and 2-hydroxy-3-butanone were identified by polarography and by v.p.c. In a control experiment, *meso*-2,3-butanediol and methyl ethyl ketone were heated with an excess of aqueous thallic ion on a steam

(32) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961); **85**, 363 (1963).

(33) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

Table IV. Derivatives

Olefin	2,4-Dinitrophenylhydrazone <sup>a</sup>		Semicarbazone <sup>b</sup>	
	M.p., °C.	M.m.p., °C.	M.p., °C.	M.m.p., °C.
<i>cis</i> -2-Butene	116.8–117.0	117.5–117.9	140.2–140.9	140.3–140.8
<i>trans</i> -2-Butene	116.8–116.9	117.2–117.5	139.9–140.5	139.6–140.1
1-Butene	114.8–115.0	114.9–115.2	140.0–141.1	140.2–141.0

<sup>a</sup> Authentic sample melted at 117.7–117.9°. <sup>b</sup> Authentic sample melted at 140.3–140.8°.

bath for 2 hr. At the end of this time, no methyl ethyl ketone was found but a 75% yield of 2-hydroxy-3-butanone (based on the amount of methyl ethyl ketone originally present) was found. By v.p.c. analysis, the glycol was found to be unchanged.

To isolate enough of the glycols for identification purposes, the oxidations with propylene, isobutene, and 1-butene were run on a 0.5-l. scale with a thallic ion concentration of 0.1 *M* in a high speed reactor to avoid secondary oxidation. The perchloric acid was neutralized with potassium carbonate to precipitate potassium perchlorate. After the salts were removed by filtering, the solution was distilled to obtain the glycol.

Propylene gave 1.6 g. of a substance boiling at 185–187° (lit.<sup>34</sup> b.p. for propylene glycol 187.4°). It was identified as propylene glycol by its infrared spectra, v.p.c. retention time which was identical with that of an authentic sample, and its phenyl urethan derivative, m.p. 143.1–143.3° (lit.<sup>35</sup> m.p. 143.4°). Isobutene gave 4.5 g. of a substance boiling at 178° (lit.<sup>36</sup> b.p. for isobutylene glycol 177–178°), which was identified as isobutylene glycol by its infrared spectra and by its molecular weight, as determined by periodic oxidation<sup>37</sup> (found 91.5; calcd. 90.12). 1-Butene gave 1.15 g. of a substance boiling at 189–190° (lit.<sup>38</sup> b.p. for 1,2-butanediol 190.5) which was identified as 1,2-butanediol by its infrared spectra, its v.p.c. retention time which was identical with an authentic sample (prepared by hydration of 1,2-epoxybutane), and its molecular weight as determined by periodic oxidation (found 93.0; calcd. 90.12). No attempt was made to isolate any glycol from the oxidation of *cis*- and *trans*-butene-2.

**Analysis of Reaction Mixtures.** The carbonyl compounds were analyzed polarographically or by vapor phase chromatography with a Carbowax 1000 column programmed from 80 to 165° at 9°/min. This system separated the aldehydes and ketones which were possible products in each reaction mixture. Before v.p.c. analysis, the reaction mixtures were neutralized with either sodium acetate or potassium carbonate. If the latter, the insolubles were filtered off and the filtrate was diluted to the original volume.

The glycols were analyzed by v.p.c. using a procedure already described<sup>2</sup> or by means of a Ucon 75 H column at 152°. Before analysis, aliquots of the reaction mix-

tures were treated with hydrochloric acid to precipitate the thallic ion and neutralized with potassium carbonate, the solids were filtered off, and the filtrate was diluted to the original volume.

To ensure that the failure to detect *meso*- or *dl*-butanediol did not result from the work-up procedure, synthetic reaction mixtures were prepared containing these glycols. These synthetic reaction mixtures were then analyzed by the usual procedure. The correct glycol analysis was always obtained.

A didecyl phthalate column at 80° was used to analyze for 1-buten-3-ol and crotyl alcohol. Neither of these two components was in the final reaction mixtures.

**Kinetic Runs.** All rates were measured by gas uptake. The ethylene and *trans*-2-butene rates could be measured at a constant atmospheric pressure as described previously.<sup>2</sup> However, the rates for the other olefins were too fast to be measured by this procedure. Therefore, for all kinetics in this study, a constant volume reactor with agitation by a gas dispersion, six-bladed turbine stirrer was employed. The stirrer was inserted into a 1-l., three-neck flask by means of a mechanical seal. One opening was used to connect to a capillary manometer and the other was used for evacuating and pressuring with gas. The stirrer speeds were about 3000 r.p.m.

The mass transfer coefficients (measured by determining rate of CO<sub>2</sub> uptake by water) indicated that rates of less than 100 *M*<sup>-1</sup> sec.<sup>-1</sup> could be measured without complication by mass transfer control when thallic ion concentrations were ca. 10<sup>-3</sup> *M* and a large excess of olefin was used. Thus, runs were made at various olefin pressures using initial thallic ion concentrations of less than 2 × 10<sup>-3</sup> *M*. Rate was measured by change in pressure. Since the pressure change during the course of a run (after initial gas uptake due to solubility) was small compared with the total pressure, the pressure was assumed to be constant, and the data were plotted as a first-order reaction. The order in olefin was determined by running at different pressures and calculating the second-order rate constant (first order in thallic ion and first order in olefin) from the Henry law constant. For all olefins, the second-order rate constant remained constant.

The Henry law constants,  $\alpha$ , for the various olefins were measured in a constant-volume reactor. Since the olefin solubility is about the same as for pure water in the low acid concentrations used in this work, the solubilities were determined in pure water to avoid the complication of olefin hydrolysis. The error in using these values of  $\alpha$  to determine the values of the second-order rate constant  $k'$  are small, since, in this range of acidities, ethylene solubility changes very little.<sup>2</sup>

(34) O. J. Schierhaltz and M. L. Staples, *J. Am. Chem. Soc.*, **57**, 2709 (1935).

(35) "Tables for Identification of Organic Compounds," 2nd Ed., The Chemical Rubber Co., Cleveland, Ohio, 1964.

(36) G. Hearne, M. Tamele, and W. Converse, *Ind. Eng. Chem.*, **33**, 806 (1941).

(37) G. O. Curme, "Glycols," Reinhold Publishing Corp., New York, N. Y., 1952, p. 337.

(38) K. A. Clendenning, F. J. MacDonald, and D. E. Wright, *Can. J. Res.*, **B28**, 610 (1950).

The values of  $\alpha$  are listed in Table V in terms of the solubility of gas at 1 mm. pressure.<sup>39</sup>

Table V. Olefin Solubilities

Olefin	Henry's law constant, $M/mm. \times 10^6$
Propylene	6.4
1-Butene	6.2
<i>cis</i> -2-Butene	9.1
<i>trans</i> -2-Butene	7.3
Isobutene	6.9

(39) The values for *cis*- and *trans*-2-butene do not agree very closely

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with those previously reported.<sup>40</sup> However, if the values for the two olefins are interchanged the agreement would be much better.

(40) M. M. Kreevoy, L. L. Schaleger, and J. C. Ware, *Trans. Faraday Soc.*, **58**, 2433 (1962).

## Calibration of the Glass Electrode in Acetonitrile. Shape of Potentiometric Titration Curves. Dissociation Constant of Picric Acid<sup>1</sup>

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An equation has been derived for the calculation of  $p_{a_H}$  in the neutralization with tetraalkylammonium hydroxide in acetonitrile of a weak acid with known dissociation constant  $K_{HA}$  and homoconjugation constant  $K_{HA_2^-}$ . The assumption was made that the tetraalkylammonium salts of the acid are completely dissociated. At 50% neutralization  $p_{a_H} = pK_{HA}$ . When the product of initial acid concentration and  $K_{HA_2^-}$  is greater than about 10, the buffer capacity has a pronounced minimum at 50% neutralization. Equations are derived to calculate  $K_{HA}$  and  $K_{HA_2^-}$  from  $p_{a_H}$ , measured with the glass electrode in mixtures of an acid and its tetraalkylammonium salt.  $pK_{HA}$  and  $pK_{2(HA)}$  of methanesulfonic acid (I) and 2,5-dichlorobenzenesulfonic acid (II) have been determined by various methods and the following values were found: 10.0 and 3.8 for I and 6.2 and 2.65 for II, respectively. The glass electrode in AN has been calibrated in mixtures of I and of II with their tetraethylammonium salts and in mixtures of *o*-nitroaniline and perchloric acid.  $pK_{HA}$  of picric acid was determined potentiometrically and a value of  $11.0 \pm 0.1$  was found. This was confirmed by spectrophotometric measurements in buffer mixtures of I and conductometric measurements in mixtures of *o*-nitroaniline and picric acid. The homoconjugation of picrate with picric acid is very slight,  $K_{HA_2^-}$  being of the order of 2.

### Introduction

The glass electrode has been used quite generally as an indicator electrode for hydrogen ions in potentiometric titrations of acids and bases in a host of organic solvents. In order to obtain from the e.m.f. the hy-

drogen ion activity, it is necessary to calibrate the glass electrode in solutions of known hydrogen ion activity. The present paper deals with the calibration of the glass electrode for  $p_{a_H}$  measurements in acetonitrile (AN) as a solvent. Several authors<sup>2,3</sup> have found the kind of glass electrode generally used for  $p_{a_H}$  measurements in aqueous medium suitable for similar measurements in AN.

Perchloric acid behaves as a strong acid in AN, but in agreement with Coetzee<sup>4</sup> we found that the potential of the glass electrode in solutions of this acid was poorly reproducible. Coetzee and Padmanabhan<sup>3</sup> calibrated the glass electrode in buffer solutions of picric acid and tetrabutylammonium picrate in which stable and reproducible potentials were measured. The  $p_{a_H}$  of the solutions was calculated from the dissociation constant of picric acid in AN, which was reported by Kolthoff, *et al.*,<sup>5</sup> to be  $10^{-8.9}$ . Later work in this laboratory revealed that this constant is considerably smaller than  $10^{-8.9}$ . In the earlier work<sup>5</sup> it was not realized that traces of impurities in the solvent have a large effect on the apparent degree of dissociation of such a weak acid.

In the present work we have made an effort to use mixtures of sulfuric acid and tetraethylammonium bisulfate for the calibration of the glass electrode. In earlier work<sup>5</sup>  $K_{HA}$  and  $K_{2(HA)}$  of sulfuric acid had been determined and, as shown below, it is possible to calculate  $a_{H^+}$  in the above mixtures. Unfortunately,

(2) J. Badoz-Lambling, J. Desbarres, and J. Tacussel, *Bull. soc. chim. France*, **53** (1962).

(3) (a) J. F. Coetzee and G. Padmanabhan, *J. Phys. Chem.*, **66**, 1708 (1962); (b) H. K. Hall, *ibid.*, **60**, 63 (1956).

(4) Private communication with Dr. J. F. Coetzee.

(5) I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **83**, 3927 (1961).