[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# Rates of Ionization of Pseudo-acids. II. Effect of Alkyl Substituents[1,2]

BY RALPH G. PEARSON AND JAMES M. MILLS

While no subject in chemistry has been more thoroughly investigated than the ionization of weak acids, the results almost always pertain to the equilibrium conditions finally established. Pseudo acids, that is, acids requiring an appreciable time to ionize, are known and both the rates of ionization and the equilibrium constants in aqueous media may be measured in many cases. If we represent a pseudo acid by HA we have

$$H_2O + HA \underset{k_2}{\overset{k_1}{\rightleftarrows}} H_3O^+ + A^- \qquad (1)$$

and $k_1/k_2 = K_{eq} = K_{ion}$ so that if $k_1$ and $K_{eq}$ are measurable, $k_2$ can also be calculated.[3] Hence fundamental information both on the kinetics of ion formation from neutral molecules and the recombination of ions can be found.

New data are presented in this paper on the rates of ionization in water of $\alpha$-ethylacetoacetic ester, methylacetylacetone, malonic ester, bromomalonic ester and ethylmalonic ester. In particular it was desired to find the effect of a simple alkyl group on the carbon atom holding the ionizable hydrogen. The method used was to measure the uptake of bromine by a conductimetric method.

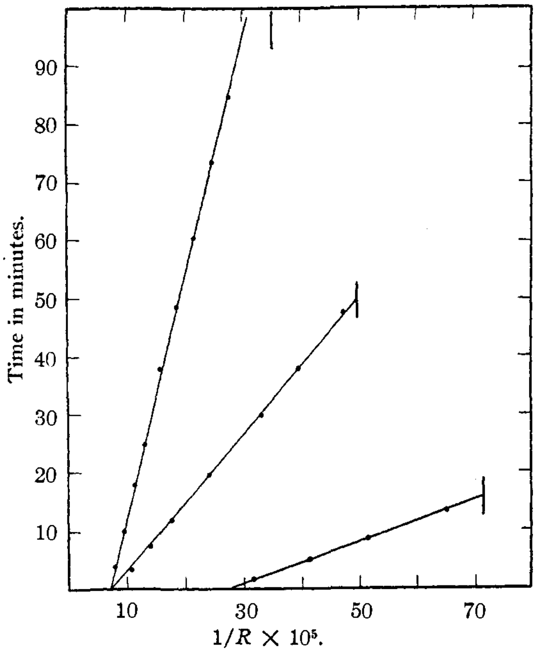

Fig. 1.—Upper, 0.03187 *M* $\alpha$-ethylacetoacetic ester, 0.00162 *M* bromine, 25°; middle, 0.0499 *M* malonic ester, 0.00466 *M* bromine, 25°; lower, 0.0330 *M* methylacetylacetone, 0.00317 *M* bromine, 25°. Vertical lines indicate 1/*R* equil.

## Experimental

Malonic ester and ethylmalonic ester were purified as previously described.[4] $\alpha$-Ethylacetoacetic ester was made by standard procedures and purified by several distillations through a ten-plate column, retaining only a small middle fraction, $n^{25}D$ 1.4198, b. p. 196° (cor.) (lit. 198°). Methylacetylacetone was made from methyl iodide and acetylacetone by the use of potassium *t*-butoxide according to Renfrow and Renfrow[5] and fractionated as above, $n^{24}D$ 1.4515, b. p. 170° (cor.) (lit. 172–173°). This material was redistilled before each use. The chief criterion of purity used for the latter two compounds was the absence of small amounts of more rapidly reacting substances as indicated by the kinetic results. The experimental condition (large excess of pseudo acid) makes the results very sensitive to such impurities and they are readily detected. Bromine water stock solutions containing small amounts of hydrobromic acid were made from bromine well washed with water and were standardized by titration for each run. Stock solutions of the organic compounds were made by weighing.

Reaction mixtures were prepared containing about 0.003 *M* bromine and the pseudo acid in large excess (10–40-fold), placed in a thermostated conductance cell and readings of the resistance made with the time starting from the time of mixing. A final reading of the resistance at equilibrium was made after a suitable time interval. Readings were made on a Jones–Josephs bridge.

## Calculations and Results

The completion of the forward reaction in (1) is followed by the very rapid reaction

$$A^- + Br_2 \xrightarrow{k_3} ABr + Br^- \qquad (2)$$

so that step (1) is the rate determining process and the rate depends only on the concentrations of pseudo acid and of water. If these are both essentially constant, we have

$$-d[HA]/dt = k_1[HA] = d[HBr]/dt \qquad (3)$$

which can be integrated to give

$$[HBr] = k_1[HA]t + [HBr]_0 \qquad (4)$$

where $[HBr]_0$ is the concentration of hydrogen bromide in the reaction mixture at $t = 0$. Since the concentration of hydrogen bromide is proportional to the reciprocal of the resistance, we should find that $1/R$ is linear with the time. Figure 1 shows the extent to which this is true. The rate constant $k_1$ can be found by extrapolating the straight line to $1/R_{equil.}$ and finding the time necessary to complete the reaction at constant rate. From this and the concentrations of bromine and pseudo acid, $k_1$ can be calculated either from

$$k_1 = \frac{1}{t_{eq.}} \frac{[Br_2]_0}{[HA]_0} \qquad (5)$$

---

[1] Presented before the Division of Physical and Inorganic Chemistry, San Francisco, California, March, 1949.

[2] For paper I of this series see Pearson, THIS JOURNAL, **70**, 204 (1948).

[3] Maron and LaMer, *ibid.*, **61**, 2018 (1939).

[4] Pearson, *ibid.*, **71**, 2212 (1949).

[5] Renfrow and Renfrow, *ibid.*, **68**, 1801 (1946).

or correcting for the change in the concentration of HA

$$k_1 = \frac{2.303}{t_{\text{eq.}}} \log \frac{[\text{HA}]_0}{[\text{HA}]_0 - [\text{Br}_2]_0} \qquad (6)$$

A correction is necessary for the amount of bromine taken up instantaneously by the enol form of the pseudo acid. This was made by measuring the conductivity of the bromine water alone at the appropriate dilution and comparing it to the conductivity of the reaction mixture extrapolated back to zero time. The difference compared to the total change in conductance gave the fraction of the bromine reacting with the enol form. Such a procedure was necessary only for methylacetylacetone, since for the other substances the concentration of enol is negligibly small.

The above treatment worked satisfactorily for α-ethylacetoacetic ester and methylacetylacetone which have only one ionizable hydrogen atom. However, malonic ester is more complicated because the bromomalonic ester which is formed by the completion of steps (1) and (2) is also a pseudo acid which ionizes and brominates to give dibromomalonic ester.

$$\text{H—CBr(COOC}_2\text{H}_5)_2 + \text{H}_2\text{O} \xrightarrow{k'_1} \bar{\text{C}}\text{Br(COOC}_2\text{H}_5)_2 + \text{H}_3\text{O}^+ \qquad (7)$$

$$\bar{\text{C}}\text{Br(COOC}_2\text{H}_5)_2 + \text{Br}_2 \xrightarrow{k'_3} \text{CBr}_2\text{(COOC}_2\text{H}_5)_2 + \text{Br}^- \qquad (8)$$

Since the bromomalonic ester ionizes more readily than malonic ester, the plot of $1/R$ against time was not truly linear but increased in slope as the concentration of bromomalonic ester increased. A kinetic analysis of a zero order reaction as in (1) followed by a first order reaction as in (7) gives the equation

$$[\text{HBr}] = 2k_1[\text{HA}]t - \frac{k_1}{k'_1}[\text{HA}](1 - e^{-k'_1 t}) + [\text{HBr}]_0 \qquad (9)$$

The procedure used was to evaluate $k_1$ from the initial slope of the $1/R$ *vs.* time plot. Then from the experimentally determined time necessary to complete the reaction, $k'_1$ can be found from (9). To prove the validity of this method the rate of reaction of bromomalonic ester was measured more directly. A malonic ester solution was prepared in which a fraction of the ester was converted to bromomalonic ester by adding bromine water and allowing to stand until equilibrium was reached.[6] A kinetic run was then made by adding more bromine water to the ester solution. The plot of $1/R$ against the time was linear, since the percentage increase in bromomalonic ester is now small, with an apparent rate constant given by

$$k_{\text{app.}} = (1 - x)k_1 + k'_1 \qquad (10)$$

where $x$ is the fraction of ester converted to bromomalonic ester. From the previously determined value of $k_1$ for malonic ester, $k'_1$ was found. Table I summarizes the results obtained in this way for malonic ester.

Ethylmalonic ester also did not give straight lines when the conductance was plotted against the time. Instead the rate fell off slowly. This may be due to the acid-catalyzed hydrolysis of the ester, an error which is greater here than for the other compounds because of the ease of hydrolysis of alkyl substituted malonic esters and because of the slowness of the ionization reaction. The rate of ionization was computed from the initial slope and cannot be regarded as very accurate. Table II gives the results obtained for all compounds together with the activation energies.

TABLE I

RATE OF IONIZATION OF MALONIC ESTER AND BROMOMALONIC ESTER

| Total ester, moles/l. | Fraction of bromoester | Bromine, moles/l. | $k_1$, min.$^{-1}$ | $k'_1$, min.$^{-1}$ |
|---|---|---|---|---|
| 0.0250 | Zero | 0.00233 | 0.00178 | 0.0092 |
| .0273 | Zero | .00333 | .00181 | .0086 |
| .0269 | Zero | .00298 | .00175 | .0086 |
| .0236 | 0.181 | .00282 | (.00178) | .0081 |
| .0157 | .070 | .00197 | (.00178) | .0081 |
| .0156 | .104 | .00193 | (.00178) | .0093 |
| .0056 | .372 | .00099 | (.00178) | .0092 |

TABLE II

RATE CONSTANTS FOR IONIZATION IN WATER

| Compound | Temp.,[a] °C. | $k_1$, min.$^{-1}$ | $E_{\text{act.}}$, kcal. |
|---|---|---|---|
| α-Ethylacetoacetic ester | 20 | $2.86 \pm .02 \times 10^{-4}$ | 15.5 |
| α-Ethylacetoacetic ester | 25 | $4.53 \pm .03 \times 10^{-4}$ | |
| α-Ethylacetoacetic ester | 35 | $10.4 \pm .2 \times 10^{-4}$ | |
| Methylacetylacetone[b,c] | 21 | $3.47 \times 10^{-3}$ | |
| Methylacetylacetone[b] | 25 | $4.97 \pm .22 \times 10^{-3}$ | 18 |
| Methylacetylacetone[b] | 35 | $1.36 \pm .09 \times 10^{-2}$ | |
| Malonic ester | 25 | $1.80 \times 10^{-3}$ | .. |
| Bromomalonic ester | 25 | $8.6 \times 10^{-3}$ | .. |
| Ethylmalonic ester | 25 | $2 \times 10^{-4}$ | .. |

[a] At least three runs were made at each temperature. [b] The amount of enol found was 3.1% at 21 and 25° and 3.8% at 35°. Nachod (reference 8) found 3.6% enol at 25° and Schwarzenbach and Felder[10] found 2.8% at 20°. [c] Only one run was made at 21°.

## Discussion

Bell and his co-workers[7] have measured the rate of water catalyzed ionization of malonic ester at 25° by the usual bromine titration method. They assumed the dibromination step to be much more rapid than the monobromination and hence, that two moles of bromine were used up each time step (1) was completed. On this basis they calculated a rate constant of 0.00142 min.$^{-1}$. This work does not support the assumption made by them since $k'_1$ is only five times as great as $k_1$. Actually the total amount of bromine reacted can be calculated about equally well with $k_1 = 0.0018$ and $k'_1 = 0.0086$ or with $k_1 = 0.00142$ and $k'_1 = \infty$ over most of Bell's experimental time range.

---

[6] Little dibromomalonic ester would be present at equilibrium because it is a brominating agent for malonic ester: Krohnke and Timmler, *Ber.*, **69B**, 614 (1936).

[7] Bell, Everett and Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A186**, 443 (1946).

Nachod[8] measured the rate of ionization of methylacetylacetone at 25° by a photometric method. He made the error of assuming that the ionization was acid catalyzed in 0.1 *N* hydrobromic acid. His results, however, can be recalculated to give a rate constant of 0.0046 min.$^{-1}$ in good agreement with the value given here. No acid catalysis has ever been observed for acids of the strength of those measured here.[9]

Table III presents a compilation of the rates of ionization of a number of pseudo acids collected from the literature, together with the acid ionization constants where known. The general trend evidently is for the rate of ionization to increase as the acidity increases. The effect of an alkyl group is generally acid weakening and rate retarding. The effect of a bromine atom is generally acid strengthening (no accurate data are known) and rate increasing.

TABLE III

RATES OF IONIZATION OF PSEUDO ACIDS AT 25°: $HA + H_2O \longrightarrow H_3O^+ + A^-$

| Compound | $k_1$, min.$^{-1}$ | $K_{\text{ion}}$ |
|---|---|---|
| Acetoacetic ester | $1.29 \times 10^{-3a}$ | $2.09 \times 10^{-11c}$ |
| α-Bromoacetoacetic ester | $1.59 \times 10^{-2a}$ | $\sim 10^{-7}$ |
| α-Ethylacetoacetic ester | $4.53 \times 10^{-4}$ | $1.84 \times 10^{-13d}$ |
| Acetylacetone | $6.8 \times 10^{-1b}$ | $1.17 \times 10^{-9c}$ |
| Methylacetylacetone | $4.97 \times 10^{-3}$ | $1.52 \times 10^{-11d}$ |
| Malonic ester | $1.80 \times 10^{-3}$ | $5 \times 10^{-14d}$ |
| Bromomalonic ester | $8.6 \times 10^{-3}$ | $\sim 10^{-9}$ |
| Ethylmalonic ester | $2 \times 10^{-5}$ | $\sim 10^{-15}$ |

[a] Pedersen, reference 9a. [b] Bell and Lidwell, *Proc. Roy. Soc.* (*London*), **A176**, 88 (1940). [c] Eidinoff, THIS JOURNAL, **67**, 2072 (1945). [d] Mills and Pearson, unpublished results.

Table IV shows values of the rate constant $k_2$ for the recombination of the ions calculated from the data in Table III. There is a trend again for the weakest acids to have the highest rates of recombination of ions. Table IV also shows the heats and entropies of activation for the forward and reverse processes of equation (1) as calculated from the transition state theory of reaction rates for those compounds where the activation energy for ionization and the heat of ionization are known. The entropies of activation for the process of ionization are always fairly large and negative and the entropies for the recombination of ions are either positive or small and negative. An explanation of this effect in terms of electrostriction of the solvent has been discussed in the first paper of this series.

TABLE IV

RATE CONSTANTS FOR THE RECOMBINATION OF IONS AT 25°: $H_3O^+ + A^- \longrightarrow HA + H_2O$

| Compound | $k_2$, l./mole-min. | $\Delta H_2,^{\ddagger}$ kcal. | $\Delta S_2,^{\ddagger}$ E. U. | $\Delta H_2,^{\ddagger}$ kcal. | $\Delta S_2,^{\ddagger}$ E. U. |
|---|---|---|---|---|---|
| Acetoacetic ester | $6.17 \times 10^{7}$ | 13.6 | −34.4 | 7.2 | −6.8 |
| α-Ethylacetoacetic ester | $2.46 \times 10^{9}$ | 14.9 | −31.6 | 7.2 | 1.0 |
| Acetylacetone | $5.81 \times 10^{8}$ | .. | .... | ... | ... |
| Methylacetylacetone | $3.27 \times 10^{8}$ | 17.4 | −16 | 9.2 | 6 |
| Malonic ester | $4 \times 10^{10}$ | .. | .... | ... | ... |

**Acknowledgment.**—This work was made possible by a grant from the Research Corporation of New York.

## Summary

The rates of ionization in water of several pseudo acids have been measured. The rates of ionization and ion recombination are correlated with ionization constants for a number of pseudo acids.

EVANSTON, ILLINOIS RECEIVED JUNE 3, 1949

---

[8] Nachod, *Z. physik. Chem.*, **A182**, 193 (1938).

[9] (a) Pedersen, *J. Phys. Chem.*, **37**, 751 (1933); (b) Junell, *Z. physik. Chem.*, **A141**, 89 (1929).

[10] Schwarzenbach and Felder, *Helv. Chem. Acta*, **27**, 1701 (1944).

---

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MONTANA STATE COLLEGE]

# The Electric Moments of Tetraethoxytitanium, Monochlorotriethoxytitanium and Trichlorophenoxytitanium in Benzene Solutions. I

BY ROBERT W. CROWE AND C. N. CAUGHLAN

Although a number of studies have been made on the dielectric properties of inorganic titanates[1] little is known about any of the physical properties of the derivatives of titanium tetrachloride containing organic groups. It has appeared worthwhile and interesting to make a somewhat detailed study of the dielectric properties of these compounds in order (a) to learn more about their structures, and (b) to find out if any of these compounds exhibit interesting and important dielectric properties. This paper represents the first report of a more extended research on the physical properties of such derivatives of titanium tetrachloride. In this work the electric moments of $Ti(OC_2H_5)_4$, $TiCl(OC_2H_5)_3$, and $TiCl_3OC_6H_5$ have been determined in benzene solution.

## Experimental

**Tetraethoxytitanium.**—This compound was easily prepared by addition of titanium tetrachloride to sodium ethoxide as described by Bischoff and Adkins.[2] The product obtained after removal of excess alcohol was purified by several distillations under reduced pressure. It is a colorless, oily liquid, $d_{25}$ 1.1066, $n^{25}_{D}$ 1.5082, b. p. 133–

---

[1] Von Hippel, Brechenridge, Chesley and Tiszo, *Ind. Eng. Chem.*, **38**, 1097 (1946).

[2] Bischoff and Adkins, THIS JOURNAL, **46**, 27 (1924).