# 388. *Ionization of Carbon–Oxygen Bonds. Part I. Ionization of Triarylmethyl Alcohols and their Alkyl Ethers in Formic Acid.*

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The ionization of various substituted triphenylmethyl alcohols in formic acid has been studied spectroscopically. The results are discussed in terms of the equilibrium (1) suggested by Hammett.

Hammett[1] suggested that triphenylmethyl alcohol ionizes in formic acid as in (1). Stewart[2] has recently examined this mechanism in some detail, and studied the kinetics of the conversion of the alcohol into triphenylmethane. His paper contains a historical discussion of the reaction.

$$\mathrm{ROH + H{\cdot}CO_2H \rightleftharpoons R^+ + H_2O + H{\cdot}CO_2^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We have made a similar study of the ionization of a number of substituted triphenylmethyl alcohols and some of their alkyl ethers. The kinetics of the conversion of the alcohols into the triphenylmethanes will be discussed later. Under our conditions, the solutions were quite stable during the period of the investigation.

## Experimental

*Formic Acid*.—(*a*) " AnalaR " 98—100% formic acid (from B.D.H.), m. p. 6·9°, was purified by the anhydrous copper sulphate method,[3] followed by three fractional crystallizations. (*b*) " AnalaR " acid (from B.D.H.) was purified solely by five fractional crystallizations. (*c*)

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[1] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, page 55.

[2] Stewart, *Canad. J. Chem.*, 1957, **35**, 766.

[3] Garner and Parker, *Amer. Chem. J.*, 1911, **46**, 236.

" AnalaR " 98—100% formic acid (from Hopkin and Williams), m. p. 5·1°, was treated as in (*a*) and in (*b*). All four samples had m. p. 8·2° and gave identical results in the ionization studies. (*d*) Repeated fractional crystallizations of a large volume of commercial acid yielded a product with m. p. 8·35°, but owing to the time involved in this preparation, most of the work described was done with formic acid of m. p. 8·2°.

*Acetic Acid.*—" AnalaR " acetic acid (2 l.) was refluxed with chromium trioxide for 12 hr., then carefully fractionated, refluxed with triacetyl borate for 12 hr., and again fractionated; the fraction of b. p. 117° was collected. The m. p. of this acid was 16·58° (lit.,[4] m. p. 16·59°).

FIG. 1*a*.

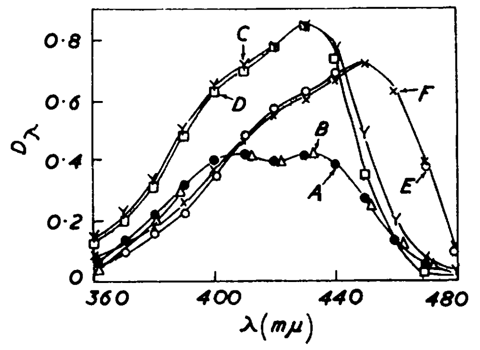

FIG. 1*b*.

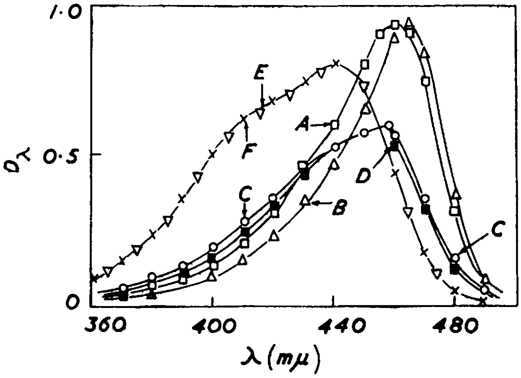

FIG. 1*a*.

*A*, ● $1{\cdot}25 \times 10^{-5}$M-Triphenylmethyl alcohol in formic acid.
*B*, △ $1{\cdot}11 \times 10^{-5}$M-Triphenylmethyl alcohol in 98% " AnalaR " $H_2SO_4$.
*C*, Y $2{\cdot}54 \times 10^{-5}$M-*p*-Fluorotriphenylmethyl alcohol in formic acid.
*D*, □ $1{\cdot}70 \times 10^{-5}$M-*p*-Fluorotriphenylmethyl alcohol in 98% $H_2SO_4$.
*E*, ○ $2{\cdot}43 \times 10^{-5}$M-*p*-Bromotriphenylmethyl alcohol in formic acid.
*F*, × $1{\cdot}53 \times 10^{-5}$M-*p*-Bromotriphenylmethyl alcohol in 98% $H_2SO_4$.

FIG. 1*b*.

*A*, □ $9{\cdot}7 \times 10^{-5}$M-Tri-*p*-chlorotriphenylmethyl alcohol in formic acid.
*B*, △ $9{\cdot}17 \times 10^{-6}$M-Tri-*p*-chlorotriphenylmethyl alcohol in 98% $H_2SO_4$.
*C*, ○ $4{\cdot}12 \times 10^{-5}$M-Di-*p*-chlorotriphenylmethyl alcohol in formic acid.
*D*, ■ $9{\cdot}38 \times 10^{-6}$M-Di-*p*-chlorotriphenylmethyl alcohol in 98% $H_2SO_4$.
*E*, ▽ $2{\cdot}35 \times 10^{-5}$M-*p*-Chlorotriphenylmethyl alcohol in formic acid.
*F*, × $1{\cdot}60 \times 10^{-5}$M-*p*-Chlorotriphenylmethyl alcohol in 98% $H_2SO_4$.

$\Delta G°$ for the ionization of tri-*p*-tolylmethyl chloride in this acid was the same as that obtained previously.[5]

*Alcohols.*—*p*-Methoxytriphenylmethyl alcohol was prepared by the standard method and recrystallized from light petroleum (b. p. 40—60°) and had m. p. 84° (lit.,[6] m. p. 84°). *p*-Hydroxytriphenylmethyl alcohol, prepared from benzophenone dichloride and phenol, was precipitated from ethanol as white platelets, m. p. 158° (lit.,[7] m. p. 159—160°), by addition of weak ammonia solution. *o*-Methyltriphenylmethyl alcohol was prepared by the standard method, m. p. 98° (lit.,[8] m. p. 98·5°). Di-*p*-chlorotriphenylmethyl alcohol, prepared by reaction of di-*p*-chlorobenzophenone and phenylmagnesium bromide in ether–benzene, was recrystallized from light petroleum (b. p. 40—60°) and had m. p. 86° (lit.,[9] m. p. 87°). The other triarylmethyl alcohols were prepared by normal methods and purified as described by Evans, Jones, and Osborne.[10] The m. p.s agree with their values.

*Ethers of Triphenylmethyl Alcohol.*—(*a*) A solution of triphenylmethyl alcohol in the appropriate alcohol was saturated with dry hydrogen chloride and refluxed for 3 hr., then set aside

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[4] Eichelberger and Latter, *J. Amer. Chem. Soc.*, 1933, **55**, 3633.
[5] Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1955, **51**, 4, 388.
[6] Kauffmann and Pannwitz, *Ber.*, 1912, **45**, 766.
[7] Cone and Robinson, *Ber.*, 1907, **40**, 2161.
[8] Boyde and Hatt, *J.*, 1927, 898.
[9] Stagner, *J. Amer. Chem. Soc.*, 1916, **38**, 2074.
[10] Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 16, 470.

overnight, whereupon the ether crystallized. (*b*) Triphenylmethyl chloride was treated with the theoretical amount of the appropriate alcoholate in excess of the alcohol as solvent. Sodium chloride was filtered off, and the ether recrystallized from the alcohol. The ethers had m. p.: methyl, 84° (lit.,[11] 84°); ethyl, 82—84° (lit.,[12] 84—85°); isopropyl 114° (lit.,[12] 114°); benzyl, 104° (lit.,[12] 103—104°).

*Spectra.*—Fig. 1 shows the spectra of solutions of triarylmethyl alcohols in formic acid and "AnalaR" 98% sulphuric acid, measured on a Unicam S.P. 500 spectrophotometer. In all cases but one there is no significant difference between the shape of the spectra in the two solvents, showing the presence of triarylmethyl carbonium ions in the formic acid solution. For the exception, tri-*p*-chlorophenylmethyl alcohol, the absorption peak occurs at 465 mμ in sulphuric acid and at 460 mμ in formic acid.

*Carbonium-ion Concentration.*—The concentrations of the carbonium ions in the formic acid solutions have been calculated by assuming their extinction coefficients to be the same as in the 98% sulphuric acid solutions, since there is a very close similarity between the spectra of the ions in these two solvent. Justification of this assumption is provided as follows. (*a*) The percentage ionizations of these alcohols and ethers in formic acid of m. p. 8·2° are given in Table 1. No alcohol shows an ionization of greater than 105%, which supports the assumption. It is further supported by the fact that the change from mono-*p*-methyltriphenylmethyl alcohol to tri-*p*-methyltriphenylmethyl alcohol causes no increase in the ionization; this shows that these alcohols must be completely ionized since in all cases where ionization is incomplete, *e.g.*, the triarylmethyl halides in nitromethane,[10] the change in substituents from mono-*p*-methyl to tri-*p*-methyl results in a very marked increase in the ionization. (*b*) We have examined the ionization of some of these alcohols in formic acid–acetic acid mixtures. Typical plots of the optical density at the peak wavelength against the mole fraction are shown in Fig. 2. For those alcohols which we find to be 100% ionized in formic acid, the optical density increases as the mole fraction of formic acid increases, up to a certain limit; this shows conclusively that after this point the alcohol is completely ionized. That the carbonium-ion concentration calculated for these completely ionized solutions is 100—105% (see Table 1) completely justifies our method of calculating these concentrations.

TABLE 1. *Ionization equilibria in formic acid* (*m. p.* 8·2°)
(*a*) *for* $C(C_6H_4R')(C_6H_4R'')(C_6H_4R''')\cdot OH$.

| R′ | R″ | R‴ | Ionization at 20° (%) | $-RT \ln \alpha$ (kcal. mole$^{-1}$) | R′ | R″ | R‴ | Ionization at 20° (%) |
|---|---|---|---|---|---|---|---|---|
| *p*-Cl | *p*-Cl | *p*-Cl | 9·4 | 1·3 | H | H | *p*-Me | 104 |
| H | *p*-Cl | *p*-Cl | 23 | 0·7 | *p*-Me | *p*-Me | *p*-Me | 103 |
| H | H | *p*-Cl | 71 | −0·5 | H | H | *o*-Me | 100 |
| H | H | *p*-F | 67 | −0·4 | *o*-Me | *o*-Me | *o*-Me | 100 |
| H | H | *p*-Br | 63 | −0·3 | H | H | *p*-OMe | 100 |
| H | H | H | 89 | −1·1 | H | H | *p*-OH | 105 |

(*b*) for $Ph_3C\cdot OAlk$.

| Alk | H | Me | Et | $Pr^i$ | $Ph\cdot CH_2$ |
|---|---|---|---|---|---|
| Ionization at 20° (%) | 89 | 91 | 88 | 86 | 84 |

With triphenylmethyl alcohol, there is no flattening-off of the optical density–mole fraction plot, which is to be expected since it is less than 100% ionized in formic acid (see Table 1).

In Fig. 3 we give the plots of optical density at the peak wavelength–mole fraction for tri-*p*-methyltriphenylmethyl alcohol of different total alcohol concentration. By plotting the optical density corresponding to the horizontal portions (plateaux), which show 100% ionization, against carbonium-ion concentration, we have verified Beer's law for these solutions. Similar straight lines are obtained for the other completely ionized alcohols.

The carbonium-ion concentrations in solutions of the ethers in formic acid have been estimated as for the alcohols. The ethers are fully ionized in 98% sulphuric acid, and all give the same spectrum whether measured in sulphuric acid or formic acid.

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[11] Hatt, *J.*, 1938, 483.

[12] Smith and Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 2400.

FIG. 2.

*A* 2·74 × $10^{-5}$M-*p*-Methoxytriphenylmethyl alcohol.
*B* 4·39 × $10^{-5}$M-Tri-*o*-methyltriphenylmethyl alcohol.
*C* 2·34 × $10^{-5}$M-*p*-Methyltriphenylmethyl alcohol.
*D* 2·09 × $10^{-5}$M-*o*-Methyltriphenylmethyl alcohol.
*E* 1·52 × $10^{-5}$M-Triphenylmethyl alcohol.

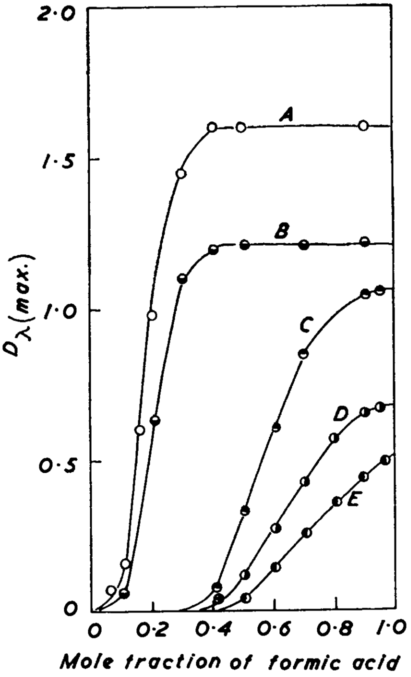
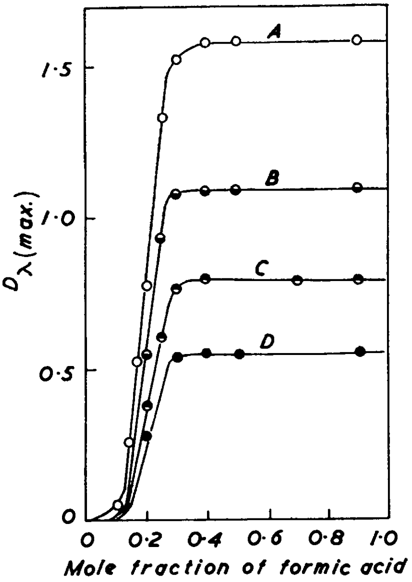


FIG. 3. *Ionization of tri-*p*-methyltriphenylmethyl alcohol in formic–acetic acid.*

*A* 2·02 × $10^{-5}$M.
*B* 1·41 × $10^{-5}$M.
*C* 1·01 × $10^{-5}$M.
*D* 7·05 × $10^{-6}$M.



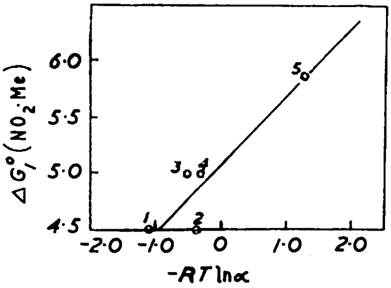


FIG. 4. *Plot of* $-RT\ln\alpha$ *for the ionization of the triarylmethyl alcohols in formic acid against* $\Delta G_i^\circ$ *for the ionization of the corresponding chlorides in nitromethane.*

| No. | R′ | R″ | R‴ |
|---|---|---|---|
| 1 | H | H | H |
| 2 | *p*-F | H | H |
| 3 | *p*-Cl | H | H |
| 4 | *p*-Br | H | H |
| 5 | *p*-Cl | *p*-Cl | *p*-Cl |

## DISCUSSION

*Nature of the Equilibrium.*—If reaction (1) correctly represents the ionisation of the triarylmethyl alcohols in formic acid, then the equilibrium constant, $K_1$, may be written

$$K_1 = \alpha[H_2O][H\cdot CO_2^-]/[H\cdot CO_2H] \text{ where } \alpha = [R^+]/[ROH]$$

The carbonium-ion concentration $[R^+]$ plotted against the concentration of un-ionized alcohol [ROH] gave good straight lines in all cases. Similar results are obtained for the ethers. $\alpha$ is therefore independent of alcohol concentration for any given alcohol. This behaviour is not predicted by reaction (1). However, our data are compatible with Hammett's equation if the remaining terms in the expression for $K_1$ do not change with alcohol concentration. Since the ionization occurs in formic acid, it is only necessary to consider changes in the concentrations of water and formate ion. The water concentration in formic acid of m. p. 8·2° is approximately $9 \times 10^{-2}$ mole $l.^{-1}$, while the formate-ion concentration, as Stewart has pointed out, is at least $10^{-3}$ mole $l.^{-1}$. Both these concentrations are much larger than that of the original alcohol ($\sim 10^{-5}$ mole $l.^{-1}$), so that the amounts of water and formate ion produced by reaction (1) are negligible, and hence reaction (1) is compatible with the observed constancy of $\alpha$.

The validity of reaction (1) can be checked by investigating the variation of $\alpha$ with variation of formate-ion concentration and water concentration. According to our expression for $K_1$, $1/\alpha$ should be proportional to the formate-ion concentration. Stewart has shown that this is so over a considerable range of concentration of formate ion, added in the form of sodium formate.

We have examined the variation of $\alpha$ when water is added to solutions of the alcohols in formic acid of m. p. 8·2°. Those which were completely ionized in this acid showed no change in ionization even when the added water had reduced the m. p. of the formic acid to 3·0°. The effect of added water on the incompletely ionized alcohols is shown in Table 2; $1/\alpha$ is approximately proportional to $[H_2O]^{1\cdot8}$, whereas reaction (1) would require a first-power dependence on water concentration.

TABLE 2. *Ionization in wet formic acid* (*all* para-*substituents*).

| R′ | R″ | R‴ | M. p.* | $[H_2O]$(M)† | Iontn.‡ | $x$ § |
|---|---|---|---|---|---|---|
| H | H | H | 2·95° | 2·41 | 9·4 | |
| | | | 5·10 | 1·46 | 30·5 | 1·74 |
| | | | 6·90 | 0·66 | 60 | |
| | | | 8·20 | 0·088 | 89 | |
| Br | H | H | 5·10 | 1·46 | 7·5 | |
| | | | 6·90 | 0·66 | 26 | 1·74 |
| | | | 8·20 | 0·088 | 63 | |
| Cl | H | H | 2·95 | 2·41 | 2·8 | |
| | | | 5·60 | 1·24 | 9·3 | 1·76 |
| | | | 7·30 | 0·49 | 35 | |
| | | | 8·20 | 0·088 | 71 | |
| Cl | Cl | H | 3·50 | 2·19 | 0·7 | |
| | | | 5·60 | 1·24 | 2·2 | 1·80 |
| | | | 7·31 | 0·49 | 11·4 | |
| | | | 8·20 | 0·088 | 23 | |
| Cl | Cl | Cl | 5·38 | 1·34 | 0·38 | |
| | | | 6·45 | 0·86 | 0·78 | 1·85 |
| | | | 7·30 | 0·45 | 2·75 | |
| | | | 8·20 | 0·088 | 9·4 | |

* M. p. of formic acid. † The acid of m. p. 8·35° being assumed anhydrous. ‡ Ionization at 20° (%). § Order in water.

There are, however, two other equilibria to be considered, both of which provide formate ions:

$$H\cdot CO_2H + H_2O \rightleftharpoons H_3O^+ + H\cdot CO_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$H\cdot CO_2H + H\cdot CO_2H \rightleftharpoons H\cdot CO_2H_2^+ + H\cdot CO_2^- \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

Both lie well to the left so that in Stewart's experiments very little of the added formate ion could be removed by either reaction's going still further to the left. Hence only reaction (1) is important and $1/\alpha$ is proportional to $[H\cdot CO_2^-]$ as observed.

On the other hand, the addition of water to the system not only suppresses the ionization of the alcohol according to reaction (1), but also has the secondary effect of increasing the $[H\cdot CO_2^-]$ according to reaction (2), which also reduces the alcohol ionization. Thus the order in water should be greater than unity. If reaction (3) may be neglected as a source of formate ion, then, assuming $[H_3O^+] = [H\cdot CO_2^-]$, we can show that

$$K_1/\sqrt{K_2} = \alpha[H_2O]^{1\cdot5}/[H\cdot CO_2H]^{0\cdot5}$$

The exponent 1·5 agrees moderately well with the observed value of 1·8. The data available do not seem reliable enough to calculate accurately the relative contributions of formate ion from reactions (2) and (3). For the incompletely anhydrous formic acid (m. p. 8·2°) used, it seems likely that reaction (2) provides about three times as much formate ion as reaction (3). This is almost certainly a lower limit. Consequently reaction (3) will have little effect.

It might be suggested that the order 1·8 found for water is due to a change in the activity coefficient of the water with change in its concentration. We have carried out experiments on the depression of the freezing point of formic acid by water over most of the range involved. The "*i*"-factors (in parentheses following molar concentrations of water) are 0·147 (0·97), 0·269 (0·94), 0·593 (0·97), 0·877 (0·90), 1·674 (0·92), and their slight decrease over this range could not account for the order of 1·8 for the effect of water on the ionisation.

As regards the ethers, R·OAlk, the analogue of reaction (1) would be:

$$\mathrm{R{\cdot}OAlk + H{\cdot}CO_2H \rightleftharpoons R^+ + HO{\cdot}Alk + H{\cdot}CO_2^-} \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

Since the water concentration, $9 \times 10^{-2}$ mole $\mathrm{l.}^{-1}$, in 8·2° m. p. formic acid, is much greater than the H·OAlk concentration can possibly be (maximum [H·OAlk] $= 10^{-4}$ mole $\mathrm{l.}^{-1}$), the carbonium ions produced in reaction (4) will rapidly equilibrate with the water present to give a state of affairs which will be little different from that of the corresponding alcohol, ROH, in formic acid. This is borne out by the fact that the percentage ionizations for the ethers of triphenylmethyl alcohol are practically the same as that for triphenylmethyl alcohol itself (see Table 1).

*Equilibrium Constants.*—It has been shown that, under our experimental conditions, the terms other than $\alpha$ in the expression for $K_1$ may be presumed constant, particularly as the same formic acid was used in all cases. Hence the value of $\alpha$ may be used as a measure of $K_1$, and $\boldsymbol{R}T \ln \alpha$ as a measure of $\Delta G_1°$.

TABLE 3. *Effect of temperature on ionization of* para-*substituted triarylmethyl alcohols.*

| R′ | R″ | R‴ | Temp. (°)<br>(α) | | | | $\Delta H_1°$ | $\delta(\Delta H_1°)$ | $\delta(-\boldsymbol{R}T \ln \alpha)$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | (kcal. mole⁻¹) | |
| Cl | Cl | Cl | 18·5<br>(0·105) | 43·0<br>(0·166) | 60·0<br>(0·23) | 75·2<br>(0·31) | 4·0 | (0) | (0) |
| H | Cl | Cl | 18·2<br>(0·32) | 44·5<br>(0·48) | 56·4<br>(0·69) | 69·4<br>(0·76) | 3·2 | 0·8 | 0·6 |
| H | H | Cl | 21·0<br>(2·2) | 47·2<br>(2·9) | 56·0<br>(3·9) | 65·5<br>(3·5) | 1·9 | 1·3 | 1·2 |
| H | H | Br | 22·0<br>(1·8) | 46·0<br>(2·1) | 56·4<br>(2·6) | 68·5<br>(3·0) | 2·2 | −0·3 | −0·2 |

The main interest centres on those alcohols which are not completely ionized at room temperature. Their behaviour is similar to that of the corresponding chlorides in nitromethane as is shown in Fig. 4, in which $\boldsymbol{R}T \ln \alpha$ is plotted against the free-energy change for the ionization of the corresponding chlorides in nitromethane. The only exception is the *p*-fluoro-compound where it is possible that ionization of the C–F bond may introduce complications.

From the variation of $\boldsymbol{R}T \ln \alpha$ with temperature for the incompletely ionized alcohols, relative values of $\Delta H_1°$ can be determined. The results are in Table 3. All these alcohols react slowly with formic acid at the higher temperatures, but in all cases the values were obtained by extrapolation to zero time. It was shown that the shape and intensity of the light-absorption curve do not vary over the temperature range used. The change in $\Delta H_1°$ is equal to the change in $(-\boldsymbol{R}T \ln \alpha)$, *i.e.*, to the change in $\Delta G_1°$. This means that the entropy change for the ionization is not affected by the change in the nature and the number of the *para*-substituents. This would be expected since the solvation shell for the ion will be far removed from the *para*-position.

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