

## The Acidities of Weak Acids. Part III.<sup>1</sup> Some 3-Benzoyl-1,1,1-trifluoroacetones

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A series of *para*- and *meta*-substituted 3-benzoyl-1,1,1-trifluoroacetones have been prepared and their acidities determined. These compounds are between 2.17 and 2.27 p*K* units more acidic than the corresponding benzoylacetones. The temperature dependence of the p*K*<sub>a</sub> values of some of the compounds serves to confirm the anomalous behaviour of the recently studied nitroparaffins, as reflected in the Δ*G*<sup>o</sup> against Δ*S*<sup>o</sup> plot.

β-DIKETONES, because of their ability to form metal complexes, are widely used for solvent extraction studies as well as for trace metal analysis. Many of their properties, including their enhanced acidity (stemming in part from the possibility of transferring negative charge from carbon to the more electronegative oxygen) have therefore been studied in detail.<sup>2</sup>

The β-difunctional system provides an excellent means of investigating the effect of structural modifications on acidity. The present study is concerned with the effect of fluorine substitution on carbon-hydrogen acidity. This is done by measuring the p*K*<sub>a</sub> values of a series of *meta*- and *para*-substituted 3-benzoyl-1,1,1-trifluoroacetones and comparing them with the values available for the corresponding benzoylacetones.<sup>3</sup>

The only previous detailed study of the effect of fluorine substitution on acidity relates to a series of substituted nitromethanes<sup>4</sup> (O<sub>2</sub>NCHXY; Y = CO<sub>2</sub>Et, CONH<sub>2</sub>, Cl, or NO<sub>2</sub>, X = Cl, H, or F). In all cases fluorine substitution led to a substantial decrease in acidity. In contrast the effect on the rates of ionisation of various carbon acids is often (but not always) to increase the rate.<sup>5,6</sup> This kind of behaviour (p*K*<sub>a</sub> increase, *k*<sub>ionis</sub> increase) although unusual, has been observed for some nitroparaffins<sup>7</sup> and some β-diketones.<sup>8</sup> In order to obtain further insight into this anomalous behaviour the temperature dependence of the acidity constants of some β-diketones have been investigated.

### EXPERIMENTAL

**Materials.**—The 3-benzoyl-1,1,1-trifluoroacetones were prepared by means of a Claisen-type condensation between ethyl trifluoroacetate and appropriately substituted acetophenones.<sup>9</sup> The latter were commercially available and were purified either by vacuum sublimation or fractional distillation. The compounds were isolated as the copper complexes before being released by steam distillation of an acid solution (10% conc. sulphuric acid) of the complex.

<sup>1</sup> Part II, D. W. Earls, J. R. Jones, and T. G. Rumney, *J.C.S. Perkin II*, 1975, 878.

<sup>2</sup> (a) M. Cox and J. Darken, *Co-ord. Chem. Rev.*, 1971, **7**, 29; (b) S. E. Livingstone, *ibid.*, p. 59.

<sup>3</sup> M. Bergon and J. P. Calnon, *Bull. Soc. chim. France*, 1972, 1020.

<sup>4</sup> H. G. Adolph and M. J. Kamlet, *J. Amer. Chem. Soc.*, 1966, **88**, 20.

<sup>5</sup> S. Andreades, *J. Amer. Chem. Soc.*, 1964, **86**, 2003.

<sup>6</sup> A. Streitwieser, jun., and D. Holtz, *J. Amer. Chem. Soc.*, 1967, **89**, 692.

Further purification was effected by either distillation or recrystallisation. The analytical data (for C, H, and, where appropriate, N) supported the assigned structure. No analysis for fluorine was made.

**p*K*<sub>a</sub> Determination.**—The procedure is similar to that given by Albert and Serjeant<sup>10</sup> and entails measuring the pH of aqueous solutions of the β-diketones (5.0 × 10<sup>-4</sup>M) that have been partially neutralised (10–90%) with carbonate-free sodium hydroxide solution (5.0 × 10<sup>-3</sup>M). The titrations were carried out under nitrogen using a glass electrode that had been previously calibrated for work in aqueous media. In each run 14–18 pH readings were taken and the p*K*<sub>a</sub> value calculated from each reading using the equation pH = p*K* + lg (*b/a* - *b*) where *b* is the concentration of the anion formed and *a* - *b*, the remaining concentration of the acid. Only in a few cases towards the end of a titration was there any noticeable drift in the p*K*<sub>a</sub> values. This could be due to the onset of hydrolysis.

Each compound was subjected to three separate p*K*<sub>a</sub> determinations and the average values, given in Tables 1 and 2 are within ±0.01–0.02 p*K* units.

### RESULTS AND DISCUSSION

Because of the low concentrations of the ketones used in determining the acidities the p*K*<sub>a</sub> values (Table 1) can be considered as true thermodynamic values. In the case of 3-benzoyl-1,1,1-trifluoroacetone for example, some determinations were carried out in a NaCl solution of ionic strength 0.1M. The value obtained (6.39 ± 0.02) is 0.15 units lower than that found in the absence of added salt, but after introduction of the activity coefficient correction a true thermodynamic value of 6.50 is obtained in good agreement with the value of 6.54 determined by using dilute ketone solutions. This is close to the average value obtained from two previous determinations<sup>11,12</sup> and 0.37 units higher than the recently reported<sup>13</sup> value in 46% (v/v) aqueous acetone solution.

<sup>7</sup> F. G. Bordwell, W. J. Boyle, jun., and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.

<sup>8</sup> J. R. Jones and S. P. Patel, *J. Amer. Chem. Soc.*, 1974, **96**, 574.

<sup>9</sup> J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.*, 1950, **72**, 2948.

<sup>10</sup> A. Albert and E. P. Serjeant, 'Ionization Constants of Acids and Bases,' Methuen, London, 1972, ch. 2.

<sup>11</sup> R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

<sup>12</sup> T. Seikine, Y. Hasegawa, and N. Ihara, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3969.

<sup>13</sup> K. Bowden, G. M. Tanner, and D. G. Tuck, *Canad. J. Chem.*, 1972, **50**, 2622.

The  $pK_a$  values given in Table 1 make no allowance for the fact that the  $\beta$ -diketones exist as tautomeric

TABLE 1

Acidity constants of substituted 3-benzoyl-1,1,1-trifluoroacetones at 298.2 K; benzoylacetone data given for comparison

No.	Substituent	$pK_a$	$pK_a$ (benzoylacetones) <sup>a</sup>
(1)	<i>p</i> -NO <sub>2</sub>	5.38	7.57
(2)	<i>m</i> -NO <sub>2</sub>	5.54	7.69
(3)	<i>m</i> -Br	6.11	
(4)	<i>p</i> -Br	6.25	8.40
(5)	<i>p</i> -Cl	6.25	8.42
(6)	<i>m</i> -OMe	6.39	8.55
(7)	H	6.39, <sup>*</sup> 6.54, 6.82, <sup>b</sup> 6.08 <sup>c</sup>	8.71
(8)	<i>p</i> -Me	6.75	8.99
(9)	<i>p</i> -OMe	6.94	9.21
(10)	<i>p</i> -OH	6.99	

\* Refers to a medium of ionic strength 0.1M.

<sup>a</sup> Ref. 3. <sup>b</sup> Ref. 11. <sup>c</sup> Ref. 12.

mixtures of the enol and keto forms. In such cases equations (1) and (2) apply where  $e$  is the fraction of enol

$$pK_E = pK_a + \lg(e) \quad (1)$$

$$pK_K = pK_a + \lg(1 - e) \quad (2)$$

present and  $pK_E$  and  $pK_K$  are the  $pK$  values for the enol and keto forms, respectively. For many  $\beta$ -diketones in water the proportion of enol is high *e.g.*  $e$  is 0.17 for acetylacetone and 0.34 for benzoylacetone.<sup>14</sup> For the fluorinated variety however the proportion is

TABLE 2

Temperature dependence of the acidity constants of some 3-benzoyl-1,1,1-trifluoroacetones

$T/K$	$pK_a^*$		
	Substituent	<i>p</i> -MeO	<i>p</i> -NO <sub>2</sub>
298.2	H	6.94	5.38
303.2		6.83	5.36
308.2		6.79	5.28
313.2		6.71	5.22
318.2		6.63	5.12
323.2		6.54	5.04

\*  $\pm 0.01$ – $0.02$ .

usually much less *e.g.* for thenoyltrifluoroacetone values of 0.020,<sup>15</sup> 0.075,<sup>9</sup> and 0.004<sup>16</sup> have been reported. This difference is a reflection of the increased importance of hydrogen bonding and hydration in the fluorinated compounds.

The benzoyltrifluoroacetones are between 2.15 and 2.27  $pK$  units more acidic than the corresponding benzoylacetones and this nearly constant difference is reflected in the similar slopes of the Hammett  $pK_a$ - $\sigma$  plots

<sup>14</sup> M. L. Eidinoff, *J. Amer. Chem. Soc.*, 1945, **67**, 2072, 2073.

<sup>15</sup> R. W. Taft, jun., and E. H. Cook, *J. Amer. Chem. Soc.*, 1959, **81**, 46.

(Figure 1). For the benzoylacetones the value is  $1.47 \pm 0.04$  and for the benzoyltrifluoroacetones  $1.38 \pm 0.03$ .

The temperature dependence of the acidity constants of the most reactive (*p*-NO<sub>2</sub>) and one of the two least reactive (*p*-OMe)  $\beta$ -diketones as well as that of benzoyltrifluoroacetone itself were studied at 5° intervals over a range of 25° (Table 2). The heats of ionisation ( $\Delta H^\circ$ ) were obtained from the slope of the  $pK_a$  against  $1/T$  plots, which, in all three cases were satisfactorily linear. The thermodynamic functions ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) for the  $\beta$ -diketones as well as the few figures available for other carbon acids are brought together in Table 3. Important

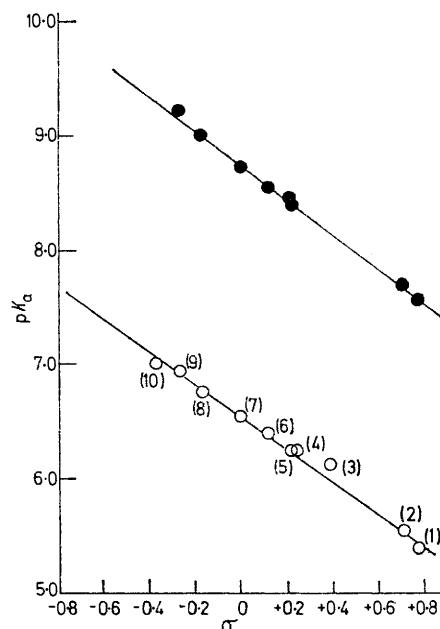


FIGURE 1 Plot of  $\beta$ -diketone  $pK_a$  values against Hammett  $\sigma$  substituent parameter:  $\circ$ , benzoyltrifluoroacetones;  $\bullet$ , benzoylacetones. For key see Table 1

differences between the results for the benzoyltrifluoroacetones and either acetylacetone or benzoylacetone can be readily seen. Thus in the former the enhanced acidity is accompanied by a factor of two increase in  $\Delta H^\circ$  (compare the cyano-compounds where increased acidity is accompanied by a drastic decrease in  $\Delta H^\circ$ ) but with a much smaller decrease in entropy, as would be expected if the fluorinated  $\beta$ -diketones are well solvated. The effect of the negative charge of the carbanion in imposing a certain ordering effect is therefore less than in the case of acetylacetone. Of the three fluorinated  $\beta$ -diketones the entropy change is least for the *p*-nitro-compound, as would be expected for a group capable of delocalisation of charge. Under these circumstances it is not surprising that  $\Delta S^\circ$  for the fluorinated  $\beta$ -diketones is close to the absolute entropy of the hydronium ion ( $-23 \text{ J K}^{-1} \text{ mol}^{-1}$ ).<sup>17</sup>

<sup>16</sup> M. R. Jaffe, D. P. Fay, M. Cefola, and N. Sutin, *J. Amer. Chem. Soc.*, 1971, **93**, 2878.

<sup>17</sup> R. W. Gurney, 'Ionic Processes in Solution,' McGraw-Hill, New York, 1953, ch. 10.

For the fluorinated  $\beta$ -diketones increasing acidity is accompanied by a decrease in  $\Delta H^\circ$  and this trend is still more apparent in the results of Boyd and Wang<sup>18</sup> on the

exception of trinitromethane, form a separate linear relationship. This difference in behaviour stems from the fact that the acidity differences in the fluorinated

TABLE 3  
Thermodynamic functions for the ionisation of some carbon acids at 298.2 K

No.	Carbon acid	$pK_a$	$\Delta G^\circ$ kJ mol <sup>-1</sup>	$\Delta H^\circ$ kJ mol <sup>-1</sup>	$\Delta S^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>	Ref.
(1)	Benzoyltrifluoroacetone	6.54	37.32	27.91	-32	a
(2)	<i>p</i> -Methoxybenzoyltrifluoroacetone	6.94	39.60	28.28	-38	a
(3)	<i>p</i> -Nitrobenzoyltrifluoroacetone	5.38	30.70	26.10	-15	a
(4)	Acetylacetone	8.93	50.96	14.85	-121	b
(5)	Benzoylacetone	8.71	49.70	(14.85) *	-117	c
(6)	Nitromethane	10.22	58.32	24.81	-112	d
(7)	Nitroethane	8.53	48.68	10.04	-130	d
(8)	2-Nitropropane	7.70	43.94	0.33	-146	d
(9)	1-Nitropropane	8.98	51.24	10.79	-136	d
(10)	Trinitromethane	-0.15	-0.85	6.66	+10	e
(11)	Malononitrile	11.20	63.9	56.1	-26	f
(12)	<i>p</i> -(Tricyanovinyl)phenyldicyanomethane	0.75	4.27	-1.67	-20	f
(13)	Methyl dicyanoacetate	-2.8	-16.0	-18.8	-10	f
(14)	Bis(tricyanovinyl)amine	-5.8	-33.0	-31.4	+6	f

\* Value assumed to be the same as that for acetylacetone.

<sup>a</sup> Present work. <sup>b</sup> J. O. Hill and R. J. Irving, *J. Chem. Soc. (A)*, 1969, 2759. <sup>c</sup> S. P. Patel, Ph.D. Thesis, University of Surrey, 1973. <sup>d</sup> T. Matsui and L. G. Hepler, *Canad. J. Chem.*, 1973, **51**, 1941, 3789. <sup>e</sup> V. I. Slovetskii, S. A. Shevelev, A. A. Fainzil'berg, and S. S. Novikov, *Zhur. Vses. Khim. obshschi im. D.I. Mendeleeva*, 1961, **6**, 599. <sup>f</sup> Ref. 18.

cyano-compounds as these have been studied over a much wider  $pK$  difference. In fact the plot of  $\Delta G^\circ$

$\beta$ -diketones and cyano-compounds result mainly from changes in  $\Delta H^\circ$ ; entropy changes play a more important role in determining the acidities of the other compounds

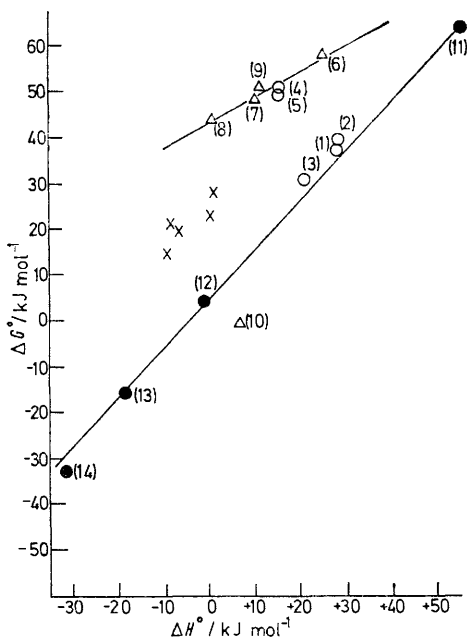


FIGURE 2 Plot of  $\Delta G^\circ$  against  $\Delta H^\circ$  for various carbon acids:  $\circ$ ,  $\beta$ -diketones;  $\Delta$ , nitroparaffins;  $\bullet$ , cyano-compounds; and  $\times$ , recently studied barbituric acids.<sup>22</sup> For key see Table 3

against  $\Delta H^\circ$  (Figure 2) for these two types of compound produces a good linear relationship, whereas the points for acetylacetone and the nitroparaffins, with the notable

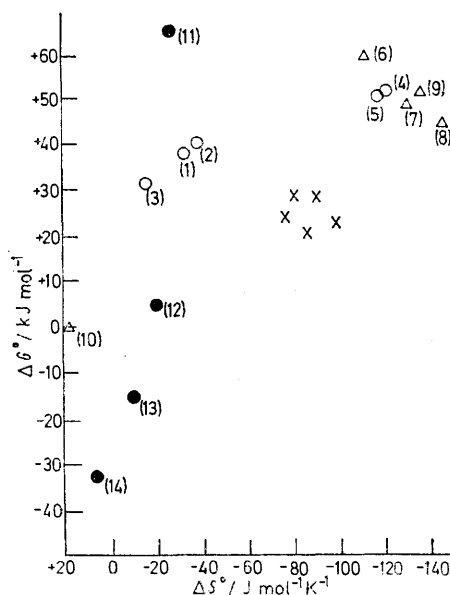


FIGURE 3 Plot of  $\Delta G^\circ$  against  $\Delta S^\circ$  for various carbon acids:  $\circ$ ,  $\beta$ -diketones;  $\Delta$ , nitroparaffins;  $\bullet$ , cyano-compounds; and  $\times$ , recently studied barbituric acids.<sup>22</sup> For key see Table 3

as can be seen more clearly from the  $\Delta G^\circ$  against  $\Delta S^\circ$  plot (Figure 3). Several studies involving carboxylic

<sup>18</sup> R. H. Boyd and C. H. Wang, *J. Amer. Chem. Soc.*, 1965, **87**, 430.

acids<sup>19</sup> and phenols<sup>20</sup> show that these two thermodynamic functions are linearly related with the weaker acids being associated with the greater entropy loss. This is true of the fluorinated  $\beta$ -diketones and cyanocompounds although the changes in  $\Delta S^\circ$  are small. However the trend for the nitroparaffins, as pointed out by Hepler,<sup>21</sup> again with the exception of trinitromethane, is in the opposite direction and the situation in the case of the 5-substituted barbituric acids<sup>22</sup> is not clear. It is interesting to note that the behaviour of trinitromethane is consistent with the view that structural and electronic rearrangement in forming the anion is considerably less than for the other nitroparaffins. The very small decrease in  $\Delta S^\circ$  for malononitrile, implying little inter-

action with the solvent and considerable charge delocalisation, is also consistent with recent kinetic investigations showing it to behave in a similar manner to oxygen and nitrogen acids of the same acidity.<sup>23</sup>

Because of the large number of activating groups available for carbon acids it is clear that no single  $\Delta G^\circ$  against  $\Delta S^\circ$  (or  $\Delta H^\circ$ ) plot will be observed but rather that the enthalpy and entropy data for different kinds of carbon acids will provide useful information on specific solute-solvent interactions and in turn lead to a better understanding of the kinetics of the ionisation process.

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<sup>19</sup> J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, 1967, **89**, 213.

<sup>20</sup> J. W. Larson and L. G. Hepler in 'Solvent-Solute Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969, ch. 1.

<sup>21</sup> T. Matsui and L. G. Hepler, *Canad. J. Chem.*, 1973, **51**, 1941.

<sup>22</sup> H. Koffer, *J.C.S. Perkin II*, 1974, 1428.

<sup>23</sup> F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, 1971, **93**, 2829.