Organic and Biological Chemistry

Weak Bases in Strong Acids. IV.[1] Basicity Scale for Carbonyl Compounds Based on Heats of Ionization in Fluorosulfuric Acid[2]

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Abstract: Some of the extensive data on base strengths of carbonyl compounds are reviewed to show the wide discrepancies between values reported for these important compounds. A different criterion for base strength $\Delta\bar{H}_{a,b}$, the heat of transfer from carbon tetrachloride to fluorosulfuric acid, is applied to 52 carbonyl bases for which clean protonation in FSO_3H has been demonstrated by nmr. A number of such spectra for protonated carbonyl bases are described here for the first time. Attempts are made to correlate the $\Delta\bar{H}_{a,b}$ values with other properties which have been proposed as criteria of base strength—the pK_a from acidity functions, carbonyl stretching frequency, COH^+ chemical shift—with varying degrees of success. Cyclopropyl and α,β-unsaturated ketones are very basic compared to aliphatic or aromatic ones, and benzaldehydes are of low basicity. Aliphatic ketones are more basic by this criterion than previous pK_a estimates suggest. Aromatic ketones for which reliable pK_a's are known fit well on the correlation line pK_a *vs.* $\Delta\bar{H}_{a,b}$ established previously for 31 amines.

In the previous paper the heat of protonation of bases in an appropriate strong acid was proposed as a criterion of base strength.[1] This suggestion was supported by measuring the enthalpies of transfer for 31 amines from carbon tetrachloride to fluorosulfuric acid. An excellent linear correlation between the enthalpies of transfer and pK_a values of the corresponding conjugate acids in water provided justification for their use as an independent measure of basicity. The application of the enthalpy basicity scale to the determination of the base strengths of carbonyl compounds is reported in this paper.

Application of the Hammett acidity function technique to determining the pK_a's of weak base "onium" ions can be weakened by failure of the analytical technique, problems in treating the data, or use of the wrong acidity function[1]—the carbonyl bases suffer from all of these shortcomings.

Confusion regarding the base strengths of carbonyl compounds is exemplified by the data in Table I. An especially serious case in point is the nine reported estimates for the pK_a of protonated acetone which span a range of seven pK_a units.[1] The lack of similar discrepancies for other carbonyl bases should not be taken as evidence that the pK_a's are known with reliability or precision—where only one attempt has been made to determine the pK_a, no conflict is possible.

Medium effects on absorption spectra are particularly serious for many carbonyl compounds. For example, the only accessible ultraviolet band for aliphatic ketones is a low-intensity (n → π^*) absorption which undergoes a substantial hypsochromic shift with increasing acid concentration.[3] The conjugate acids of carbonyl compounds often exhibit absorption maxima which are also medium dependent and not well separated from the free base peak.[4] The apparent pK_a which is estimated from such data is also quite sensitive to the correction technique used to compensate for medium effects.

Table I. Literature Values for pK_a's of Several Carbonyl Bases

Compd	$-$pK_a
Acetophenone	3.65,[a] 4.12,[a] 6.24,[b] 6.36,[c,d] 6.42,[e] 6.51,[f] 7.00,[g] 7.82,[h] 7.99[h]
Benzaldehyde	4.40,[a] 4.87,[a] 6.63,[h] 6.87,[h] 7.35,[b] 7.39,[g] 7.48,[i] 7.90[g]
Benzophenone	3.90,[a] 4.01,[a] 6.19,[j] 5.7,[k] 6.38,[l] 6.41,[m] 6.42,[h] 8.0,[h] 8.42[h]

[a] R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, **46**, 2469 (1968). [b] Values of G. Culbertson and R. Petit (*J. Amer. Chem. Soc.*, **85**, 741 (1963)) corrected to the acidity function of M. J. Jorgenson and D. R. Hartter, *ibid.*, **85**, 878 (1963). [c] Values of L. A. Flexer, L. P. Hammett, and A. Dingwall (*ibid.*, **57**, 2103 (1935)) corrected to the acidity function of Jorgenson and Hartter.[b] [d] R. Stewart and K. Yates (*ibid.*, **80**, 6355 (1958)), corrected to the acidity function of Jorgenson and Hartter.[b] [e] E. M. Arnett, T. Cohen, A. A. Bothner-By, R. D. Bushick, and G. Sowinski, *Chem. Ind.* (London), 473 (1961), corrected to the acidity function of Jorgenson and Hartter.[b] [f] P. Haake, P. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967). [g] K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965). [h] C. C. Greig and C. D. Johnson, *J. Amer. Chem. Soc.*, **90**, 6453 (1968). [i] K. Yates and R. Stewart (*Can. J. Chem.*, **37**, 664 (1959)), corrected to the acidity function of Jorgenson and Hartter.[b] [j] T. Handa and M. Kobayashi, *Yuki Gosei Kagaku Kyokai Shi*, **13**, 580 (1955); *Chem. Abstr.*, **51**, 8439 (1957), corrected to the acidity function of Jorgenson and Hartter.[b] [k] T. G. Bonner and J. Philips, *J. Chem. Soc., B*, 650 (1966). [l] R. Stewart, M. R. Granger, R. B. Moodie, and L. J. Muenster (*Can. J. Chem.*, **41**, 1065 (1963)), corrected to the acidity function of Jorgenson and Hartter.[b] [m] A. Fisher, B. A. Grigor, J. Packer, and J. Vaughan, *J. Amer. Chem. Soc.*, **83**, 4208 (1961).

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(1) Previous paper in this series: E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Amer. Chem. Soc.*, **92**, 1260 (1970).

(2) Supported by National Science Foundation Grant No. GP-6550X.

(3) H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960).

(4) N. C. Deno, *Surv. Progr. Chem.*, **2** (1964).

Thus, Greig and Johnson[5] reported that aromatic carbonyl group protonations do *not* follow the amide acidity function, H_A; conversely, Zalewski and Dunn[6] have concluded that the protonation behavior of aromatic carbonyl compounds *does* follow H_A. For benzophenone, acetophenone, and benzaldehyde this difference of opinion results in an average discrepancy of 3.3 pK_a units in the values reported by the two groups.

Such ambiguity in determining base strengths is a serious matter for a class of compounds as important as the carbonyl bases. Accurate knowledge of the equilibrium protonation behavior of carbonyl compounds is required for structure–reactivity correlations and for detailed kinetic analysis of acid-catalyzed reactions. For these reasons we were attracted to the carbonyl bases as the next area in which to extend the basicity scale which we have proposed, based on heats of protonation in FSO_3H at 25°.

Evidence that representative carbonyl bases are cleanly converted to their conjugate acids in superacid media at low temperature is provided by the nmr studies of Olah,[7] Gillespie,[8] Winstein,[9] Hogeveen,[10] Brouwer,[11] Deno, and others.[12] Supplementary nmr evidence documenting simple protonation of many more carbonyl compounds in FSO_3H at room temperature is reported in this paper.

Experimental Section

Materials. Most of the compounds used in this study were available commercially. Liquids were generally dried, using an appropriate agent, and then distilled. Solids were recrystallized and dried. Some were purified by vacuum sublimation. All melting points, boiling points, and refractive indices were in good agreement with literature values. Carbon tetrachloride and fluorosulfuric acid were purified as described previously.[1] Diphenylcyclopropenone, mp 119.5–121.5° (lit.[13] mp 119–120°), was synthesized according to the method of Breslow, *et al.*[13] 4-Dichloromethyl-4-methylcyclohexa-2,5-dienone, mp 52–53° (lit.[14] mp 52.5°), was prepared according to the method of Vitullo.[14] 2,3:6,7-Dibenzocycloheptatrien-1-one, mp 88–89° (lit.[15] mp 88.4:89.2°), was prepared by the method of Cope and Fenton.[15] Anthrone, mp 154–157° (lit.[16] mp 154–155°), was synthesized according to the procedure of Meyer.[16]

Methods. Nmr spectra were determined with a Varian A-60 nmr spectrometer. All chemical shifts (δ) are reported in parts per million (ppm) downfield from TMS using either internal CH_2Cl_2 (δ 5.30[9a]) or $(CH_3)_4NCl$ (δ 3.10[17]) as secondary standards in FSO_3H. Samples of protonated ketones for nmr observation were prepared by adding slowly the internal standard and *ca.* 50 mg of ketone to a rapidly stirred solution of 0.5 ml of FSO_3H in a 2-dram vial at room temperature. These solutions were then quickly transferred *via* pipet to an nmr sample tube whose plastic cap had been punctured to prevent the build-up of pressure. The calorimeter equipment and procedures are basically as described previously.[1,18]

Results

The heats of solution of carbonyl compounds in CCl_4 ($\Delta\bar{H}_{CCl_4}$) and in FSO_3H ($\Delta\bar{H}_{FSO_3H}$) at 25° are listed in Table II along with other structural parameters. As discussed in previous articles,[1,19] the heat of solution in CCl_4 has been used to correct the heat of solution in FSO_3H for the energy associated with separating the solution molecules. The process represented by $\Delta\bar{H}_{a,b}$ refers to the heat of transfer of the compound from a dilute solution in CCl_4 to FSO_3H, which we will refer to as the heat of protonation.

The nmr spectra of representative carbonyl bases in FSO_3H at room temperature were examined to document the protonation process and the stabilities of the conjugate acids. The observation of simple conversion to protonated species under conditions used for the nmr studies (0.1–1.0 *M*, 40°) is taken as good evidence for similar behavior under the conditions of the calorimetric measurements (*ca.* 10^{-3} *M*, 25°). The following compounds were examined by nmr in FSO_3H at room temperature and their spectra are reported.

The nmr spectrum of acetone in FSO_3H at 40° consists of a sharp singlet methyl resonance at δ 3.12. The nmr spectrum of cyclobutanone in FSO_3H at 37° consists of an unsymmetrical triplet at δ 3.85 (J = 7.5 Hz) and a quintuplet at δ 2.60 (J = 7.5 Hz) with relative areas of 1.9–1.0. The nmr spectrum of cyclopentanone in FSO_3H at 40° consists of two multiplets centered at δ 3.24 and 2.38 with relative areas of 1.0–1.0. The nmr spectrum of 2-adamantanone in FSO_3H at 40° exhibits absorptions at δ 3.27, 2.80, 2.60, and 2.17 in approximate relative areas of 2:1:6:4. These spectra are in good agreement with the published spectra of Olah[7c,g] in FSO_3H–SbF_5–SO_2 at −60°.

The nmr spectrum of crotonaldehyde in FSO_3H at 40° exhibits a doublet at δ 9.10 which overlaps with a multiplet centered at 8.72 (combined area two) as well as another multiplet centered at 7.08 (relative area one) and a doublet at 2.64 (relative area three). The nmr spectrum of dicyclopropyl ketone in FSO_3H at 40° consists of a multiplet centered at δ 2.15. The nmr spectrum of 4-dichloromethyl-4-methylcyclohexadienone in FSO_3H exhibits an apparent AB quartet centered at δ 7.74, a singlet at 6.00, and another singlet at 1.72. Integration of the peaks gave the expected 4:1:3 ratios.

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[5] See Table I, footnote *h*.

[6] See Table I, footnote *a*.

[7] (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **90**, 6087 (1968); (b) G. A. Olah and R. H. Schlosberg, *ibid.*, 90, 6464 (1968); (c) G. A. Olah and M. Calin, *ibid.*, 90, 400, 405, 938, 4672 (1968); (d) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967); (e) G. A. Olah and M. Calin, *ibid.*, **89**, 4736 (1967); (f) G. A. Olah and A. M. White, *ibid.*, **89**, 3591, 4752 (1967); (g) G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582, 3586 (1967); (h) G. A. Olah and C. U. Pittman, *ibid.*, **88**, 3310 (1966); (i) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 5123 (1965).

[8] (a) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965); (b) R. J. Gillespie and T. Birchall, *ibid.*, **41**, 148, 2642 (1963).

[9] (a) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967); (b) G. C. Levy and S. Winstein, *ibid.*, **90**, 3574 (1968); (c) G. C. Levy, Ph.D. Thesis, University of California, 1968.

[10] (a) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. MacLean, *Rec. Trav. Chim. Pays-Bas*, **86**, 687 (1967); (b) H. Hogeveen, *ibid.*, **86**, 289, 696, 809 (1967); (c) H. Hogeveen, *ibid.*, **87**, 1295, 1305, 1313 (1968).

[11] (a) D. M. Brouwer, *ibid.*, **86**, 879 (1967); (b) D. M. Brouwer, *Tetrahedron Lett.*, 453 (1968); (c) D. M. Brouwer, *Chem. Commun.*, 515 (1967).

[12] (a) N. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. S. Wisotsky, *J. Amer. Chem. Soc.*, **84**, 2016 (1962); (b) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963); (c) J. L. Sudmeier and K. E. Schwartz, *Chem. Commun.*, 1646 (1968); (d) R. van der Linde, J. W. Dornseiffen, J. U. Veenland, and Th. J. de Boer, *Spectrochim. Acta*, **24A**, 2115 (1968); (e) Th. J. Sekuur and P. Kranenburgh, *Tetrahedron Lett.*, 4769, 4793 (1966); (f) C. MacLean and E. L. Mackor, *J. Chem. Phys.*, in press.

[13] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

[14] V. P. Vitullo, *J. Org. Chem.*, **34**, 224 (1969).

[15] A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, **73**, 1673 (1951).

[16] K. H. Meyer in "Organic Synthesis," Coll. Vol. IV, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1941, p 60.

[17] H. G. Richey and R. K. Lustgarten, *J. Amer. Chem. Soc.*, **88**, 3136 (1966). (Other workers have recently used δ 3.20 for this standard.)

[18] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *ibid.*, **87**, 1541 (1965).

[19] E. M. Arnett and J. W. Larsen, *ibid.*, **91**, 1438 (1969).

The nmr spectrum of mesityl oxide in FSO_3H at 40° consists of singlets at δ 6.80, 2.82, 2.70, and 2.53 with relative areas of 1:3:3:3. These spectra are in excellent agreement with published spectra for crotonaldehyde in FSO_3H–SbF_5 at −20°,[11b] dicyclopropyl ketone in 96% H_2SO_4 at 40°,[7i] 4-dichloromethyl-4-methylcyclohexadienone in 90.5% H_2SO_4 at 35°,[14] and mesityl oxide in HF–SbF_5 at −60°.[11b]

The nmr spectrum of benzaldehyde in FSO_3H at 40° contains a singlet at δ 9.54 and an aromatic multiplet centered at 8.15 with relative areas of 1:5. The nmr spectrum of *p*-nitrobenzaldehyde consists of a singlet at δ 9.95 and a narrow aromatic multiplet centered at 8.66 with relative areas of 1:4. The nmr spectrum of 2,4,6-trimethylbenzaldehyde in FSO_3H at 40° exhibits peaks at δ 9.64, 7.36, 2.80, and 2.60 with relative areas of 1:2:6:3. The nmr spectrum of benzaldehyde is in good agreement with the spectrum observed by Levy at −52° in SO_2–FSO_3H–SbF_5.[9c]

The nmr spectrum of acetophenone in FSO_3H at 40° consists of a broad aromatic multiplet at δ 8.10 and a sharp singlet at 3.40 with relative areas of 5:3. The nmr spectrum of *p*-nitroacetophenone in FSO_3H at 40° exhibits a narrow aromatic multiplet centered at δ 8.60 and a sharp singlet at 3.57 with relative areas of 4:3. The nmr spectrum of 2,4,6-trimethylacetophenone in FSO_3H at 40° consists of a relatively broad singlet at δ 7.18, a singlet at 2.85, a doublet centered at 2.66, and a singlet at 2.40 with relative areas of 1:3:6:3. The nmr spectrum of 4-acetylbiphenyl in FSO_3H at 40° contains a complex aromatic multiplet centered at δ 8.18 and a singlet at 3.33 with relative areas of 3:1. The nmr spectrum of 4-acetylfluorene in FSO_3H at 40° is composed of a complex aromatic multiplet centered at δ 8.24, a broad singlet at 4.23, and a sharp doublet at 3.32 with relative areas of 7:2:3. The nmr spectra for acetophenone and *p*-nitroacetophenone are in excellent agreement with published spectra in FSO_3H at −82 and −84°, respectively.[8a]

The nmr spectrum of 2,3:6,7-dibenzocycloheptatrien-1-one in FSO_3H at 40° contains apparent doublets centered at δ 8.86 and 8.20 with other smaller peaks under the high-field doublet. The nmr spectrum of coumarin in FSO_3H at 40° consists of an apparent doublet centered at δ 8.85, a complex aromatic multiplet centered at 7.86, and another doublet centered at 7.16 with relative areas of 1:4:1, although the two outside doublets resemble an AB splitting pattern. The nmr spectrum of 2,6-dimethyl-4-pyrone in FSO_3H at 40° exhibits sharp singlets at δ 6.94 and 2.72 with relative areas of 1:3. The nmr spectrum of 2,3:6,7-dibenzocycloheptatrien-1-one is in excellent agreement with the spectrum observed by Levy at −50° in FSO_3H–SbF_5.[9c]

The nmr spectrum of *p*-methylbenzophenone in FSO_3H at 40° consists of a complex aromatic multiplet centered at δ 7.85 and a singlet at 2.62 with relative areas of 3:1. The nmr spectrum of 4,4′-dimethylbenzophenone in FSO_3H at 40° contains an AB splitting pattern in the aromatic region centered at δ 7.66 and a singlet at δ 2.60 with relative areas of 4:3. The nmr spectrum of 4,4′-dimethoxybenzophenone in FSO_3H at 40° exhibits two aromatic multiplets centered at δ 8.30 and 7.44 and methoxyl group singlets at 4.35 and 4.23 with relative areas of 4.7:3.3:3.6:3.2.

Discussion

The enthalpies of protonation of carbonyl bases in fluorosulfuric acid listed in Table II are proposed as a criterion for their base strength by analogy with our establishment of such a scale for amines.[1] The correlation of the heats of protonation for 31 amines with their aqueous $\mathrm{p}K_a$ values gave an excellent linear relationship (correlation coefficient 0.992), which was described by eq 1. It was proposed that this enthalpy–

$$-\Delta\bar{H} = (1.78\ \mathrm{p}K_a + 28.1)\ \text{kcal/mol} \qquad (1)$$

free energy correlation could be used to estimate the base strengths of other classes of compounds.

The carbonyl bases are not an ideal series to test the applicability of this correlation, but we know of no better one presently available. Reported values for the $\mathrm{p}K_a$'s of carbonyl bases referred to dilute aqueous solution are not unequivocal because of the problems associated with their variable acidity function dependence and the inability to correct unambiguously for medium effects on their spectra as the acidity changes. However, we feel that the $\mathrm{p}K_a$ estimates of Stewart and his coworkers for benzaldehydes,[20] acetophenones,[21] and diaryl ketones[22] are self-consistent; thus, relative basicities within each group should be meaningful. It should be emphasized that his estimates may not all be referred accurately to the dilute aqueous reference state. Comparison of the enthalpy basicity scale with Stewart's $\mathrm{p}K_a$ estimates should provide another test of the general consistency of the former. These $\mathrm{p}K_a$ estimates are listed in column five of Table II along with those from different sources for several other compounds. These $\mathrm{p}K_a$ values and their differences should be compared with the heats of protonation listed in the fourth column of Table II and with estimated $\mathrm{p}K_a$ values (column six) calculated from eq 1 and the corresponding enthalpies. In Figure 1 are presented the $\Delta\bar{H}_{a,b}$ for a number of aromatic and conjugated carbonyl compounds whose $\mathrm{p}K_a$'s are also listed in Table II. Most of them are taken from the work of Stewart's group[20–22] because of their scope and self-consistency. The correlation line included on this graph was generated from eq 1 based upon the data for amines. The standard deviation of calculated $\mathrm{p}K_a$'s (eq 1) from the literature values is 1.0 $\mathrm{p}K_a$ unit, which attests to the consistency of the enthalpy basicity scale.

Another structural parameter which has proved to be very useful in correlating reactivity in various reaction series is the carbonyl stretching frequency. Thus, in addition to the Foote–Schleyer solvolysis rate–ν_{CO} relationship,[23] several correlations of $\mathrm{p}K_a$'s with infrared carbonyl stretching frequencies have been reported for families of carbonyl compounds.[20–22] Values for carbonyl stretching frequencies are listed in the seventh column of Table II and a plot of $\Delta\bar{H}_{a,b}$ *vs.* carbonyl stretching frequency is shown in Figure 2. Naturally, in view of the dispersion of ν_{CO} *vs.* $\mathrm{p}K_a$ plots and the linearity of $\Delta\bar{H}_{a,b}$ *vs.* $\mathrm{p}K_a$ plots, separate correlations for each class of carbonyl base are found.

Birchall and Gillespie[8a] have reported a linear correlation between $\mathrm{p}K_a$ and the chemical shift of the CO^+H

(20) See Yates and Stewart, Table I, footnote *i*.
(21) See Stewart and Yates, Table I, footnote *d*.
(22) See Stewart, *et al.*, Table I, footnote *l*.
(23) (a) See Table II, footnote *s*; (b) see Table II, footnote *t*.

Table II. Structural Parameters and Thermodynamic Quantities for Protonation of Carbonyl Compounds in FSO_3H at 25°

No.	Compd	$\Delta\bar{H}_{CCl_4}$[a]	$-\Delta\bar{H}_{FSO_3H}$[b]	$-\Delta\bar{H}_{a,b}$[c]	$-pK_a$ lit.	$-pK_a$ calcd[dd]	$\nu_{C=O}$, cm^{-1}	Ionization potential, eV	δ_{COH^+},[d] ppm
	Aliphatic Ketones								
1	Hexachloroacetone	0.22 ± 0.09	−2.14 ± 0.08	−1.92 ± 0.1		14.7			
2	Cyclobutanone	0.57 ± 0.03	13.8 ± 0.3	14.4 ± 0.3	10.5[e]	7.7	1791[s]		14.73,[gg] 14.9[jj]
3	Cyclododecanone	3.99 ± 0.2	12.0 ± 0.3	16.0 ± 0.4		6.8	1713[s]		
4	Cyclodecanone	−0.20 ± 0.03	17.1 ± 0.2	16.9 ± 0.2		6.3	1704[s]		
5	2-Norbornanone	0.61 ± 0.14	16.5 ± 0.3	17.1 ± 0.3		6.2	1751[s]		13.75,[gg] 14.1[jj]
6	Cyclopentanone	0.32 ± 0.02	17.3 ± 0.1	17.6 ± 0.1	8.0[e]	5.9	1740[t]		14.17,[gg] 14.7[jj]
7	Adamantanone	1.40 ± 0.1	16.2 ± 0.3	17.6 ± 0.3		5.9	1727[s]		13.85[jj]
8	Cyclohexanone	0.09 ± 0.01	18.1 ± 0.1	18.2 ± 0.1	7.1[e]	5.6	1716[s]		14.03,[gg] 14.1[jj]
9	Cycloheptanone	0.06 ± 0.06	18.1 ± 0.2	18.2 ± 0.2	6.9[e]	5.6	1705[s]		13.93,[gg] 13.8[jj]
10	2-Pentanone	0.43 ± 0.01	18.4 ± 0.2	18.8 ± 0.2		5.2	1720[u]	9.39[ee]	14.30,[kk] 14.16[kk]
11	Acetone	0.79 ± 0.02	18.3 ± 0.1	19.1 ± 0.1	7.6[e]	5.1	1718,[s] 1719[u]	9.69[ff]	14.24,[gg] 14.93[kk]
12	Crotonaldehyde	0.90 ± 0.04	18.6 ± 0.9	19.5 ± 0.9	4.32,[f] 4.35[f]	4.8	1696[v]	9.73[ff]	
13	Dicyclopropyl ketone	0.06 ± 0.02	20.7 ± 0.2	20.8 ± 0.2		4.1	1694[w]		12.08[gg]
	Unsaturated Ketones								
14	4-Dichloromethyl-4-methylcyclohexadienone	5.49 ± 0.2	15.8 ± 0.2	21.3 ± 0.3	3.44[g]	3.8	1670[g]		
15	Mesityl oxide	0.24 ± 0.08	23.7 ± 0.3	23.9 ± 0.3		2.4	1697[v]	9.05[ff]	
	Aldehydes								
16	4-Nitrobenzaldehyde	5.71 ± 0.09	7.98 ± 0.2	13.7 ± 0.2	9.2[h]	8.1	1713[x]		15.57[hh]
17	3-Nitrobenzaldehyde	7.27 ± 0.31	7.03 ± 0.82	14.3 ± 0.9		7.8			15.22[hh]
18	Benzaldehyde	0.91 ± 0.01	15.2 ± 0.1	16.1 ± 0.1	7.5[h]	6.7	1710,[y] 1708[x]	9.51[ff]	13.29[gg]
19	4-Isopropylbenzaldehyde	0.68 ± 0.02	15.8 ± 0.1	16.5 ± 0.1		6.5	1705[x]		
20	4-Methylbenzaldehyde	0.91 ± 0.04	16.2 ± 0.3	17.1 ± 0.3	6.6[h]	6.2			
21	2,4,6-Trimethylbenzaldehyde	0.90 ± 0.05	17.4 ± 0.2	18.3 ± 0.2	4.7[i]	5.5			
	Aromatic Ketones								
22	3-Chloroacetophenone	1.13 ± 0.01	15.3 ± 0.2	16.4 ± 0.2	7.4[j]	6.6	1696[z]		
23	4-Chloroacetophenone	1.04 ± 0.03	16.1 ± 0.1	17.1 ± 0.1	6.8[j]	6.2	1692,[z] 1694[x]		13.52[ii]
24	2,4,6-Trimethylacetophenone	0.54 ± 0.04	16.7 ± 0.8	17.2 ± 0.8	8.4[i]	6.1			
25	3-Nitroacetophenone	7.12 ± 0.43	10.8 ± 0.2	17.9 ± 0.4	8.0[j]	5.7	1701,[z,u] 1703[x]		14.75[hh]
26	4-Nitroacetophenone	7.52 ± 0.35	11.2 ± 0.3	18.7 ± 0.5	8.5[j]	5.3	1700[z]		15.33[ii]
27	Acetophenone	0.79 ± 0.01	18.1 ± 0.2	18.9 ± 0.2	6.4[j]	5.2	1691,[z] 1692,[y] 1693[x]	9.57[ee]	13.46,[ii] 13.03[gg]
28	3-Methylacetophenone	0.78 ± 0.02	18.2 ± 0.6	19.0 ± 0.6	6.2[j]	5.1			
29	3-Methoxyacetophenone	0.83 ± 0.06	19.8 ± 0.1	20.6 ± 0.1	7.0[j]	4.2			
30	1-Acetylnaphthalene	1.21 ± 0.05	16.8 ± 0.3	18.0 ± 0.3	5.41,[k] 5.09[k]	5.7			
31	2-Acetylnaphthalene	5.68 ± 0.1	12.4 ± 0.3	18.1 ± 0.3	5.71[k]	5.6			
32	3-Acetylbiphenyl	7.24 ± 0.3	29.4 ± 0.3	36.6 ± 0.4		−4.8			
33	2-Acetylfluorene	7.15 ± 0.1	31.2 ± 0.5	38.4 ± 0.5		−5.8			
34	Fluorenone	4.5 ± 0.2	9.7 ± 0.3	14.2 ± 0.4	7.0[l]	7.8	1730[aa]		12.67[hh]
35	2,3:6,7-Dibenzocycloheptadienone	0.89 ± 0.11	15.6 ± 0.08	16.5 ± 0.1	5.8[1]	6.5			11.61[hh]
36	2,3:6,7-Dibenzocycloheptatrienone	6.0 ± 0.1	12.8 ± 0.2	18.8 ± 0.2	5.2[l]	5.2	1660[l]		10.97[hh]
37	Anthrone	6.5 ± 0.4	12.7 ± 0.3	19.2 ± 0.5	5.0[1]	5.0	1678[aa]		11.48[hh]
38	Coumarin	6.11 ± 0.1	13.5 ± 0.2	19.6 ± 0.2		4.8			
39	Xanthone	5.6 ± 0.3	15.0 ± 0.2	20.6 ± 0.4	4.1[m]	4.2	1674[m]		
40	Diphenylcyclopropenone	5.22 ± 0.2	18.7 ± 0.3	23.9 ± 0.4	2.5[n]	2.4	1640[n]		11.03[hh]
41	2,6-Dimethyl-4-pyrone	6.23 ± 0.24	25.2 ± 0.2	31.4 ± 0.3	−0.40,[o] −0.38[p]	−1.8	1639[bb]		
42	4,4-Dichlorobenzophenone	6.42 ± 0.12	8.49 ± 0.2	14.9 ± 0.2	7.3[l]	7.4	1670[u]		
43	4-Chlorobenzophenone	5.38 ± 0.2	10.2 ± 0.4	15.6 ± 0.4	6.9[l]	7.0	1666[u]		
44	4-Bromobenzophenone	5.49 ± 0.4	9.64 ± 0.3	15.1 ± 0.5		7.3	1665[u]		
45	Benzophenone	5.26 ± 0.25	11.6 ± 0.2	16.9 ± 0.3	6.4[l]	6.3	1664[u]	9.00[v]	12.23[gg]
46	4-Methylbenzophenone	4.86 ± 0.2	12.9 ± 0.2	17.8 ± 0.3		5.8	1661[u]		
47	4,4′-Dimethylbenzophenone	5.48 ± 0.08	12.6 ± 0.2	18.1 ± 0.2	5.8[1]	5.6	1659[u]		
48	4-Methoxybenzophenone	6.1 ± 0.2	14.1 ± 0.1	20.2 ± 0.2		4.4	1658[u]		
49	4,4′-Dimethoxybenzophenone	8.58 ± 0.51	21.5 ± 1.5	30.1 ± 1.8	4.4[l]	−1.1			
	Other Carbonyl Bases								
50	Ethyl benzoate	0.36 ± 0.02	14.1 ± 0.1	14.5 ± 0.1	7.8[q]	7.6	1721[y]		
51	Ethyl acetate	0.014 ± 0.004	17.4 ± 0.1	17.4 ± 0.1		6.0	1745[y]	10.10[ff]	
52	Benzoyl chloride	0.72 ± 0.1	5.3 ± 0.5	6.0 ± 0.5	11.2[r]	12.4	1778[cc]		

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[a] The heat of solution of the pure compound into CCl_4 in kilocalories per mole. [b] The heat of solution of the pure compound into FSO_3H in kilocalories per mole. [c] The heat of transfer from CCl_4 to FSO_3H in kilocalories per mole. [d] The chemical shift of the CO^+H proton at low temperature in superacid media. [e] Reference 3, corrected to the H_0 scale of Jorgenson and Hartter (see Table I, footnote *b*). [f] Reference 6. [g] Reference 14. [h] Yates and Stewart (Table I, footnote *i*), corrected to the H_0 scale of Jorgenson and Hartter (Table I, footnote *b*). [i] W. M. Schubert and R. E. Zahler, *J. Amer. Chem. Soc.*, **76**, 1 (1954); M. A. Paul and F. A. Long, *Chem. Rev.* **57**, 1 (1957). [j] Stewart and Yates

Table II. Footnotes (*continued*)

(Table I, footnote *d*), corrected to the H_0 scale of Jorgenson and Hartter (Table I, footnote *b*). [k] Reference 5. [l] Stewart, *et al.* (Table I, footnote *l*), corrected to the H_0 scale of Jorgenson and Hartter (Table I, footnote *b*). [m] A. I. Tolmachev, L. M. Shulezhko, and A. A. Kisilenko, *Russ. J. Gen. Chem.*, **35**, 1708 (1965). [n] Reference 13. [o] N. F. Hall, *J. Amer. Chem. Soc.*, **52**, 5115 (1930). [p] H. K. Rördam, *ibid.*, **37**, 557 (1915). [q] Value of J. Hine and R. P. Bayer, *ibid.*, **84**, 1989 (1962), corrected to the scale of Jorgenson and Hartter (Table I, footnote *b*). [r] M. Liler, *J. Chem. Soc.*, *B*, 205 (1966). [s] C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964). [t] P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964). [u] N. Fuson, M. Josien, and E. M. Shelton, *ibid.*, **76**, 2526 (1954). [v] D. Cook, *ibid.*, **80**, 49 (1958). [w] H. Hart and O. E. Curtis, *ibid.*, **78**, 112 (1956). [x] H. W. Thompson, R. W. Needham, and D. Jameson, *Spectrochim. Acta*, **9**, 208 (1957). [y] G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953). [z] R. N. Jones, W. F. Forbes, and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957). [aa] T. C. Bruice and A. B. Sayigh, *J. Amer. Chem. Soc.*, **81**, 3416 (1959). [bb] D. Cook, *Can. J. Chem.*, **39**, 1184 (1961). [cc] M. S. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948). [dd] Calculated from $\Delta \bar{H}_{a,b}$ using eq 1 in text. [ee] J. D. Morrison and A. J. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952). [ff] K. Watanabe, *ibid.*, **26**, 542 (1957). [gg] Reference 9a. [hh] Reference 9c. [ii] Reference 8a. [jj] Reference 7c. [kk] Reference 7g.

proton at low temperatures in FSO_3H. Winstein[9] and Olah[7c,g] have determined the CO^+H chemical shift for many protonated ketones in other superacid media. These data are listed in column nine of Table II and a plot of $\Delta \bar{H}_{a,b}$ *vs.* CO^+H chemical shift is shown in Figure 3. Although a definite trend toward decreasing chemical shift with increasing basicity is evident, this parameter does not correlate satisfactorily with the enthalpy–basicity scale and the limited data available do not permit resolution into correlations for separate families.

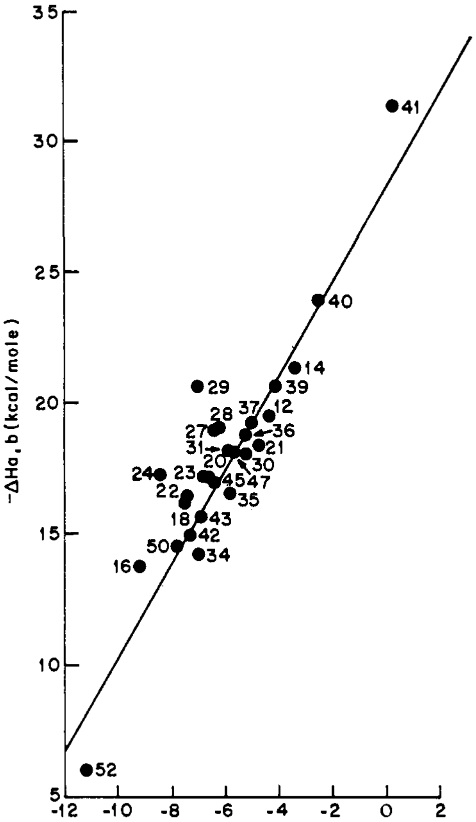

Figure 1. Heats of protonation for various aromatic and conjugated carbonyl compounds in FSO_3H *vs.* pK_a values of their conjugate acids in water. $\Delta \bar{H}_{a,b}$ for compounds **24** and **29** probably contain other contributions in addition to simple protonation (see text).

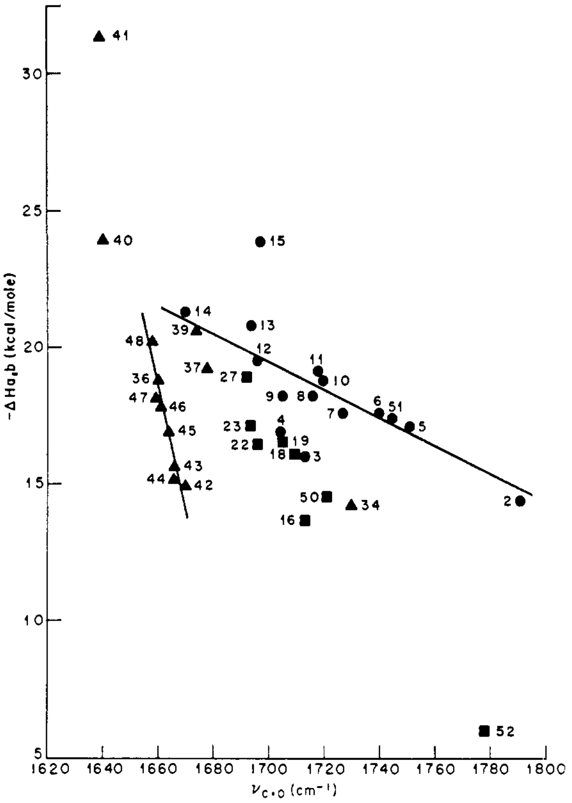

Figure 2. Heats of protonation of carbonyl compounds in FSO_3H *vs.* carbonyl stretching frequencies: ●, aliphatic carbonyl bases; ■, benzaldehydes and acetophenones; ▲, diaryl and other aromatic ketones.

The available data for the ionization potentials of carbonyl bases are listed in column eight of Table II.

In the following sections the relationships between these structural parameters and $\Delta \bar{H}_{a,b}$ are discussed more thoroughly for each class of carbonyl base.

Saturated Aliphatic Ketones. Saturated aliphatic ketones exhibit a range of $\Delta \bar{H}_{a,b}$ from +1.92 kcal/mol for hexachloroacetone to −19.1 kcal/mol for acetone. The relative heats of protonation of the alicyclic ketones fall in the same order as the pK_a estimates of Campbell and Edward determined spectrophotometrically, although our pK_a estimates (from eq 1) are much higher than those reported by them. The standard deviation of our calculated pK_a's from those of Campbell and Edward[3] is 2.4 pK_a units. Deno's studies by Raman and nmr[24] spectroscopy support their observation that acetone is half-protonated in about 80% sulfuric acid. We can suggest three possible reasons for the failure of our correlation to accommodate these bases: (a) the high concentrations of these bases needed for *all* of the spectroscopic methods used so far impose extraneous

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(24) N. C. Deno and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **85**, 1735 (1963).

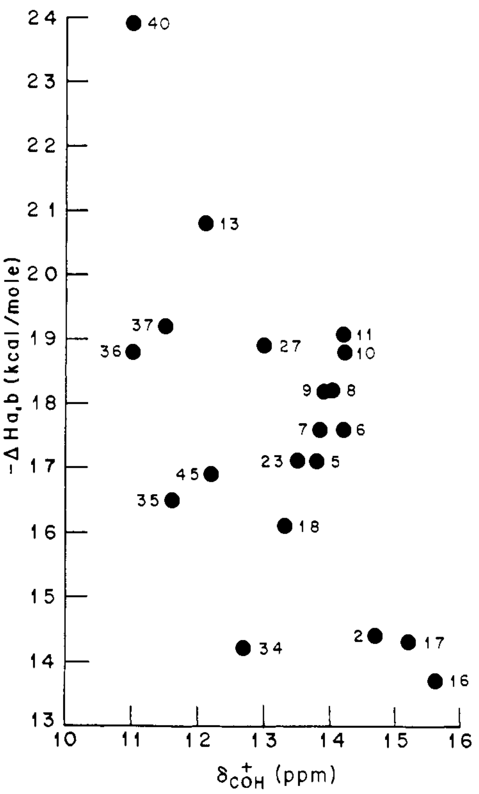

Figure 3. Heats of protonation of carbonyl compounds in FSO_3H *vs.* the chemical shift of the CO^+H proton.

medium effects on the apparent indicator ratio. (b) The small internal pressure effects of these simple aliphatic molecules cause them to follow a different acidity function from the aromatic ketones. The influence of this factor on the activity coefficients might cause a serious discrepancy in the lengthy extrapolation to the dilute aqueous standard state. (c) The proportionality constants in the fundamental extrathermodynamic relations[1] which define the requirements for a true $\Delta\bar{H}_{a,b}$ *vs.* pK_a correlation may be quite different for aliphatic and aromatic ketones. It is important that some technique be found to measure the pK_a's of these ketones at high dilution in aqueous acid in view of their extensive use in the analysis of acid-catalyzed reaction kinetics.[25]

The increase in basicities of aliphatic ketones parallels a corresponding decrease in the carbonyl stretching frequency of the conjugate base as shown in Figure 2. This correlation is satisfactory except for cyclododecanone and cyclodecanone. These compounds show unusual behavior in their reactivity which has been attributed to their conformational requirements.[26] Increasing basicity for aliphatic ketones roughly parallels a decrease in the chemical shift of the CO^+H proton. The large difference in ionization potentials for acetone and 2-pentanone eliminates that property as a useful guide to Brønsted basicity for these bases.

The nmr spectra of cyclobutanone, cyclopentanone, acetone, and 2-adamantanone in FSO_3H at 40° were examined carefully to establish the protonation process and indicated clean conversion to the corresponding conjugate acid in each case.

Unsaturated Carbonyl Bases. The cyclopropyl and α,β-unsaturated ketones are much more basic than the saturated aliphatic ones. Clean conversion to protonated base in FSO_3H at 40° was established by nmr for each compound in this class shown in Table I, thus ruling out exothermic side reactions as the cause of their apparent high basicity on this enthalpy scale. The relatively high pK_a estimates for these compounds support the recent determinations of Zalewski and Dunn,[27] and these compounds fall exactly on the $\Delta\bar{H}_{a,b}$–pK_a correlation line for the amines in Figure 1. The relatively low CO^+H chemical shift for dicyclopropyl ketone seems to be in accord with its relatively high basicity. Crotonaldehyde and 4-dichloromethyl-4-methylcyclohexadienone fall on the $\Delta\bar{H}_{a,b}$–ν_{CO} correlation line for aliphatic ketones, while mesityl oxide is far from this line. The lower basicity of crotonaldehyde relative to 4-dichloromethyl-4-methylcyclohexadienone and mesityl oxide is an indication of the lower basicity of aldehydes relative to ketones. We were unable to quantify this prediction due to the observed rapid decomposition of aliphatic aldehydes in FSO_3H at 40° as shown by nmr. The CO^+H chemical shifts of aliphatic aldehydes occur at lower fields than aliphatic ketones.

Benzaldehydes. The basicities of benzaldehydes tend to be low relative to the other types of carbonyl bases listed in Table II. The relative basicity order and the effect of substituents is consistent with the pK_a estimates of Stewart[20] for these compounds as shown in Figure 1. Our calculated basicities tend to be *ca.* 1 pK_a unit higher than those of Stewart except for 2,4,6-trimethylbenzaldehyde whose pK_a was determined in another study by Schubert.[28] These deviations might be a reflection of the documented failure of benzaldehydes to follow the H_0 function defined for primary aniline indicators.[5,6,29,30] An increase in basicity in this series corresponds to a decrease in carbonyl stretching frequency and a decrease in the CO^+H chemical shift.

Clean conversion to protonated species in FSO_3H at 40° was established by nmr for 4-nitrobenzaldehyde, 4-methylbenzaldehyde, 2,4,6-trimethylbenzaldehyde, and benzaldehyde.

Acetophenones. In general, the basicities of substituted acetophenones follow the orders predicted on the basis of Stewart's[21] pK_a's, carbonyl stretching frequencies, and CO^+H chemical shifts. The standard deviation of calculated pK_a's from literature pK_a's is 1.2 pK_a units (see below) and all the acetophenones appear to be more basic on the enthalpy basicity scale.

The data for acetophenones provide excellent examples of how the failure to follow the expected orders can be used to detect questionable basicity values. The difference between calculated pK_a's and literature values for 2,4,6-trimethylacetophenone (**24**), 4-nitroacetophenone (**26**), 3-nitroacetophenone (**25**), and 3-methoxyacetophenone (**29**) are greater than three times the standard deviations of other carbonyl bases from estimated values. Consistent with this method of diagnosis, 2,4,6-trimethylacetophenone does not under-

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[25] (a) P. Greenzaid, Z. Luz, and D. Samuel, *Trans. Faraday Soc.*, 64, 2787 (1968); (b) M. Byrn and M. Calvin, *J. Amer. Chem. Soc.*, **88**, 1916 (1966); (c) D. Samuel and B. L. Silver, *Advan. Phys. Org. Chem.*, 3, 123 (1965); (d) G. Aksnes, D. Aksnes, and P. Albrikstsen, *Acta Chem. Scand.*, 20, 1325 (1966).

[26] (a) J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962); (b) N. J. Leonard, *Rec. Chem. Progr.*, 17, 243 (1956); (c) V. Prelog, *ibid.*, **18**, 247 (1957).

[27] R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, **47**, 2263 (1969).

[28] See Table II, footnote *i*.

[29] See Jorgenson and Hartter, Table I, footnote *b*.

[30] See Table I, footnote *g*.

go simple carbonyl protonation in FSO_3H at 40° as indicated by the observation of four methyl resonances in the nmr spectrum. The anomalously exothermic heats of protonation of 3- and 4-nitroacetophenone and 3-methoxyacetophenone are probably due to specific exothermic interaction of the substituent with solvent (*i.e.*, H bonding or complete proton transfer). This interpretation is reasonable in view of the high acidity of FSO_3H ($H_0 = -13.9$[31]) and the considerable heat of protonation of the weakly basic nitrobenzene in FSO_3H (6.6 kcal/mol[1]). Protonation of the nitro group has been observed by nmr for nitromesitylene in FSO_3H–SbF_5 at −84.5°,[8a] *p*-nitrophenylacetone in FSO_3H–SbF_5 at −70°,[9b] and nitrobenzene in HF–BF_3 at −100°.[32]

Previous explanations of the *low* basicity for *m*-alkoxy-substituted acetophenones were given in terms of solvent-substituent hydrogen bonding in aqueous sulfuric acid.[21] Conversely, such exothermic hydrogen bonding interactions would be expected to lead to *high* basicity estimates founded on heats of protonation. Recent nmr chemical shift variations for anisoles[33a] and *p*-fluoronitrobenzenes[33b] in solvents of varying acidity are in accord with these speculations. The behavior of anisole in strong acids at room temperature is a subject of current controversy.[34] The failure to observe similarly high basicity estimates for nitro-substituted benzaldehydes is consistent with the evidence discussed by Stewart[20] indicating more steric hindrance to solvation and/or resonance in the acetophenone series than in the benzaldehyde series. The extraordinarily high heats of solution in FSO_3H observed for 4-acetylbiphenyl and 2-acetylfluorene are excellent indications of decomposition for these substrates. The nmr spectrum of 2-acetylfluorene in FSO_3H at 37° showed two methyl resonances confirming this explanation. The nmr spectra of acetophenone and *p*-nitroacetophenone were clean and consistent with simple carbonyl protonation.

Polycyclic Aromatic Ketones. These bases provide a good test of the accuracy of the enthalpy basicity scale for carbonyl compounds. Stewart[22] reported that plots of indicator ratios *vs.* H_0 gave slopes near unity for them indicating that they are probably "good" Hammett bases. If this is so, the estimated pK_a values can be safely referred to dilute aqueous standard state. It is reassuring, therefore, to note that $\Delta\bar{H}_{a,b}$ for these compounds follow the amine $\Delta\bar{H}_{a,b}$–pK_a correlation line very well (see Figure 1). The relative order of enthalpy basicities is in agreement with CO^+H chemical shifts, but the carbonyl stretching frequency correlation is poor. The high basicity estimate for 2,6-dimethyl-4-pyrone may be an indication of processes other than simple carbonyl protonation, although no evidence for either ring protonation or ether–oxygen interaction was seen in its nmr spectrum in FSO_3H at 40°. Clean and simple nmr spectra were also observed for 2,3:6,7-dibenzocycloheptatrienone and coumarin. The effects of conformational nuances on the observed basicities of these compounds have been discussed expertly by Stewart.[22]

Benzophenones. The estimated pK_a's for benzophenones are in excellent agreement with those reported by Stewart[22] as shown in Table II and Figure 1. This agreement can be regarded as either definitive or fortuitous, however, because of the present extreme disagreement regarding the appropriate acidity function for protonation of these compounds in aqueous acid as discussed in the introductory statement. An excellent linear correlation of protonation heats for the benzophenones *vs.* the corresponding carbonyl stretching frequencies is shown in Figure 2.

The unusually high basicity estimate for 4,4′-dimethoxybenzophenone indicates that this compound is undergoing rapid side reactions in FSO_3H. This was confirmed by the observation of two methoxyl resonances in its nmr spectrum in FSO_3H at 40°. By analogy with the nmr studies of other substituted benzophenones,[9a,12b,c] fast proton exchange at carbonyl oxygen should be occurring under these experimental conditions. Thus, we attribute the nonequivalence to either protonation or sulfonation of one of the aromatic rings.[9b,34]

The nmr spectra of 4-methylbenzophenone and 4,4′-dimethylbenzophenone (singlet methyl resonance) were clean and consistent with oxygen protonation in FSO_3H at 40°.

Conclusions. The heats of protonation of carbonyl bases in FSO_3H give an order of basicity which is generally in agreement with other basicity and structural parameters. A number of aromatic and unsaturated ketones and aldehydes fit quite closely to the excellent correlation between heats of protonation of amine bases and their aqueous pK_a values.[1] For such carbonyl bases of unknown pK_a, we propose that the enthalpies presented in column four of Table II provide a useful estimate of basicity provided they are cleanly protonated in FSO_3H. For saturated ketones, the correlation is poor and the cause of the discrepancy is uncertain at this time. The protonation process in FSO_3H at 40° has been documented for many of the compounds studied and the results are in good agreement with low-temperature spectra in other superacid media. The enthalpy–basicity scale does not rely on any extrapolation; all of the enthalpies presented in column four of Table II have a common standard state of infinite dilution in carbon tetrachloride. Several generalizations regarding the effect of structure on basicity of carbonyl compounds can be made.

(1) The most basic carbonyl compounds are α,β-unsaturated bases and those which can form Hückel "$4n + 2$" systems upon protonation (*e.g.*, diphenylcyclopropenone and 2,6-dimethyl-4-pyrone). These bases have calculated pK_a's in the range of −2 to −5.

(2) Aromatic carbonyl bases whose phenyl rings can approach coplanarity with the protonated carbonyl group have pK_a values in the region of −5.

(3) Strain-free aliphatic ketones appear to be surprisingly basic on this enthalpimetric scale. The pK_a (−5) which would be estimated for acetone makes it as basic as anthrone and acetophenone in contrast to the results of other workers.

(4) Aromatic carbonyl bases have pK_a's in the range −5 to −8. Within this range, the relative order of basicities is acetophenones ≫ benzophenones > benzaldehydes. Although the weakly basic character of

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(31) R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968).

(32) H. Hogeveen, *Rec. Trav. Chim. Pays-Bas*, **87**, 1320 (1967).

(33) (a) R. G. Wilson and D. H. Williams, *J. Chem. Soc., C*, 2475 (1968); (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963).

(34) B. G. Ramsey, *ibid.*, **88**, 5358 (1966).

benzaldehydes is generally accepted, the markedly increased basicity of acetophenones relative to benzophenones is a new observation and worthy of further documentation.[35] This order seems to be a manifestation more of the electron-withdrawing inductive effects of phenyl substituents in the "onium" ion than of their potential electron-donating conjugative ability and is also evident from comparison of the heat of protonation of ethyl acetate (−17.4 kcal/mol) with ethyl benzoate (−14.5 kcal/mol). Conjugative stabilization in the free base would also give the same order. Taft[36] concluded, on the basis of fluorine nmr shielding effects in substituted benzophenones, that thermodynamic substituent effects are the resultants of substantial effects in both complexed ($\bar{\rho} = -7.00$ for H_2SO_4 adduct) and uncomplexed ($\bar{\rho} = -2.43$) ketone. The observed order acetone $\approx$ acetophenone $\gg$ benzophenone tends to eliminate π-complex interaction of the phenyl ring with FSO_3H as an important contributing factor to the high basicity estimates for aromatic carbonyl compounds on this scale. The opposite order would be expected if these interactions were significant.

(5) Within the alicyclic ketone series, increasing ring strain is manifested in a decrease in basicity. Thus, a difference of 4 kcal/mol in heats of protonation exists between cyclohexanone and cyclobutanone.

(6) Fluorenone, which would produce a potentially antiaromatic cation,[37] is one of the weakest bases examined, even though it possesses the potential for conjugation with two coplanar phenyl rings in the conjugate acid.

(7) The very low basicity of benzoyl chloride and hexachloroacetone bears witness to the dramatic sensitivity of the basicity of carbonyl compounds to inductive effects.

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(35) One of us (*J. W. L.*) has observed this order in several other systems. Extension of Dewar's SCF-MO calculations for conjugated molecules to this series might be interesting. See M. J. S. Dewar and T. Morita, *J. Amer. Chem. Soc.*, **91**, 802 (1969).

(36) P. G. Pews, Y. Tsuno, and R. W. Taft, *ibid.*, **89**, 2391 (1967).

(37) (a) R. Breslow, H. W. Chang, R. Hill, and E. Wassermann, *J. Amer. Chem. Soc.*, **89**, 1112 (1967); (b) R. Breslow, *Angew. Chem. Intern. Ed. Engl.*, **7**, 565 (1968); (c) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 3727 (1961); (d) R. Breslow, J. Brown, and J. Gajewski, *ibid.*, **89**, 4383 (1967).

Calculation of Partial Mass Spectra of Some Organic Compounds Undergoing Competing Reactions from the Molecular Ions

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Abstract: Methyl *o*-toluate, methyl salicylate, *p*-chloroaniline, nitrobenzene, and diethyl ketone each undergo two important reactions from their molecular ions, one involving rearrangement and the other formally corresponding to a simple bond cleavage. These reactions are treated as competing unimolecular reactions within the framework of the quasi-equilibrium theory (QET). To preserve mathematical simplicity, an empirical modification is made to the original and simplest QET equation relating the rate constant (k) and internal energy (E), in the hope that this will compensate for inadequacies of the original equation near threshold. Treating only the frequency factors for the rearrangement reactions as adjustable parameters, good agreement is obtained between calculated and observed partial mass spectra of methyl *o*-toluate, methyl salicylate, and *p*-chloroaniline. It is suggested that the QET may be applied in calculation of the mass spectra of organic compounds in general, at least up to the degree of functional complexity considered in the present paper.

Interpretation of the mass spectra of organic compounds has during the last 10 years proceeded almost entirely on empirical grounds.[1,2] Notable exceptions are, however, found in calculation of the mass spectra of simple hydrocarbons, such as propane, by means of the quasi-equilibrium theory (QET).[3–6] The application of this theory to complex organic molecules containing heteroatoms has been questioned[1,7] and organic chemists have not applied its principles in attempts to calculate ion abundances in mass spectra. This paper deals with the partial calculation of simple mass spectra of some organic molecules, where hitherto only empirical interpretations have been available.[8]

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(1) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

(2) J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier Publishing Co., Amsterdam, The Netherlands, 1968.

(3) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

(4) H. M. Rosenstock and M. Krauss in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 1.

(5) H. M. Rosenstock in "Advances in Mass Spectrometry," Vol. 4, E. Kendrick, Ed., The Institute of Petroleum, London, 1968, pp 523–545; see also M. L. Vestal in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 2.

(6) For calculations of the mass spectra of hydrocarbons and simple monofunctional compounds, see (a) A. Kropf, E. M. Eyring, A. L. Wahrhaftig, and H. Eyring, *J. Chem. Phys.*, **32**, 149 (1960); (b) E. M. Eyring and A. L. Wahrhaftig, *ibid.*, **34**, 23 (1961); (c) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *ibid.*, **37**, 1276 (1962); (d) L. Friedman, F. A. Long, and M. Wolfsberg, *ibid.*, **27**, 613 (1957); (e) J. Collin, *Bull. Soc. Roy. Sci. Liege*, **7**, 520 (1956); (f) A. B. King and F. A. Long, *J. Chem. Phys.*, **29**, 374 (1958); (g) W. A. Chupka, *ibid.*, **30**, 191 (1959); (h) W. A. Chupka and J. Berkowitz, *ibid.*, **32**, 1546 (1960); (i) B. Steiner, C. F. Giese, and M. G. Inghram, *ibid.*, **34**, 189 (1961); (j) W. A. Chupka and M. Kaminsky, *ibid.*, **35**, 1991 (1961).

(7) G. Spiteller and M. Spiteller-Friedmann, *Justus Liebigs Ann. Chem.*, **690**, 1 (1965).