THE PROTONATION OF THE CARBONYL GROUP

III. DIARYL KETONES

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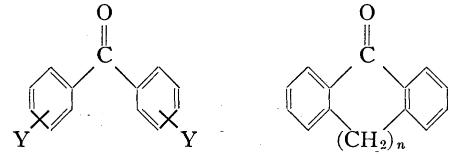
ABSTRACT

The basicities of 14 diaryl ketones have been determined. Except for 4,4′-bis(dimethylamino)benzophenone, which protonates on nitrogen, the pK_{BH^+} values range from -4.19 for 4,4′-dihydroxybenzophenone to -10.12 for 4,4′-dinitrobenzophenone. The basicities are not correlated well by either σ or σ^+ substituent constants and it is believed that this is due either to a variation in the degree of rotation (and hence conjugation) of the two aryl rings or to a departure of carbonyl basicities from the conventional acidity scale based on ammonia bases. The effect on the basicity of joining the ortho positions by bridges of various sizes has also been determined and the results are discussed in terms of steric and electronic effects.

Previous work in this laboratory has been concerned with the protonation of very weakly basic groups such as carbonyl (1), carboxyl (2, 3), and carboxamido (4, 5). We now wish to report the basicities of two series of diaryl ketones. In one series the para or meta substituents in benzophenone are varied and in the other the angle of the aryl rings with the carbonyl group is varied by means of ortho–ortho bridges.

$$\mathrm{Ar_2C{=}O} + \mathrm{H^+} \rightleftharpoons \mathrm{Ar_2C{=}\overset{+}{O}H}$$



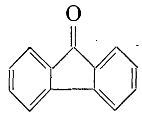
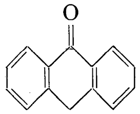
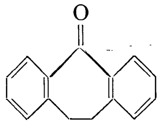
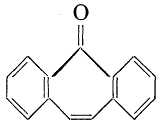
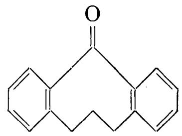
The basicities of benzophenone and anthrone have been previously measured by Handa and Koboyashi (6) and those of benzophenone and some of its alkyl derivatives by Fischer, Grigor, Packer, and Vaughan (7).

RESULTS AND DISCUSSION

The basicities and the ultraviolet spectral data for the diaryl ketones are given in Table I. Unlike the series of monoaryl ketones and aldehydes (1) whose basicities correlate quite well with the modified Hammett substituent constants, σ^+ (8), the present series (compounds I to VIII) does not give a very satisfactory fit with any of the parameters commonly used in linear free energy correlations. This may be due to the presence of two potentially conjugating rings each of which can rotate and whose actual degrees of conjugation may vary considerably with the identity of the para substituents. Another possibility to be considered is that carbonyl compounds are not following the conventional Hammett acidity function, H_0, which is based on protonation of amine bases (9, 10). The satisfactory correlations with σ^+ previously observed for benzaldehydes and acetophenones do not cover nearly the range of acidities spanned by the benzophenones. Recent work suggests that the anomalous ionization curves often obtained with carbonyl bases are due less to solvent effects on spectra than to the compounds' ionization not following the function H_0 (9). It should be pointed out in this connection that most of the

TABLE I

pK_{BH^+} and ultraviolet spectral data for diaryl ketones

		Basicity		Neutral compound*		Conjugate acid†		
Compound		pK_{BH^+}	% H_2SO_4 at half ionization	λ_{max} (mμ)	$10^{-4}\epsilon_{max}$	λ_{max} (mμ)	$10^{-4}\epsilon_{max}$	$\Delta\lambda$ (mμ)
$(C_6H_5)_2C{=}O$	(I)	-6.16‡	73.8	258	1.70	344 292	2.44 1.36	86
$(p\text{-}CH_3C_6H_4)_2C{=}O$	(II)	-5.67	70.0	273	1.96	375 302	3.90 1.27	102
$(p\text{-}CH_3OC_6H_4)_2C{=}O$	(III)	-4.39	59.5	299 225	2.20 1.28	404 319 246	4.30 1.06 0.67	105
$(p\text{-}HOC_6H_4)_2C{=}O$	(IV)	-4.19	57.6	300 230	2.10 1.30	390 305 240	3.74 0.97 0.67	90
$(p\text{-}ClC_6H_4)(C_6H_5)C{=}O$	(V)	-6.64	77.6	267	2.05	363 299	3.30 1.20	96
$(p\text{-}ClC_6H_5)_2C{=}O$	(VI)	-6.96	80.0	264§	2.60	377 311	4.24 1.50	(113)
$(m\text{-}NO_2C_6H_4)_2C{=}O$	(VII)	-9.85‖	99.3	258¶	2.81	322**	2.05	64
$(p\text{-}NO_2C_6H_4)_2C{=}O$	(VIII)	-10.12‖	99.6	280¶	2.70	324**	1.74	44
	(IX)	-6.65	77.6	257	8.3	266	5.3	9
	(X)	-5.02	64.7	275	1.5	351	2.4	76
	(XI)	-5.69	70.2	276	1.3	358	2.3	82
	(XII)	-5.25	66.6	262	4.0	293	9.1	31
	(XIII)	-5.80	71.1	277	1.3	353	2.5	76

*Solvent is $EtOH\text{–}H_2O$ (1:10).

†Solvent is 95% H_2SO_4.

‡Literature values, -5.5 (6) and -6.18 (7).

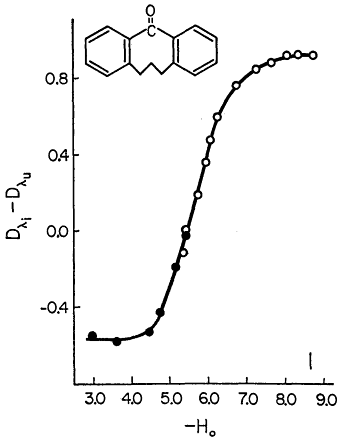
§The low solubility of this compound required the use of 95% EtOH.

‖The pK_{BH^+} of nitrobenzene is -11.26 (J. C. D. Brand, J. Chem. Soc., 997, (1950)); the nitro groups in the ketones will be less basic than this and so carbonyl, not nitro, protonation must be occurring here.

¶Solvent is 80% H_2SO_4.

**Solvent is 30% fuming H_2SO_4, nitro protonation has probably occurred here.

compounds studied in the present work gave excellent ionization curves with slopes very near unity for the logarithmic plots (Figs. 1 and 2). Following the suggestions of Professors N. C. Deno and E. M. Arnett (personal communications) we have also listed in



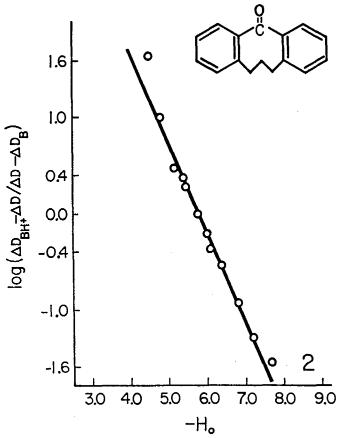


FIG. 1. The function $D\lambda_i - D\lambda_u$ plotted against $-H_0$ for 2,3;7,8-dibenzcyclooctadienone (XIII). $\lambda_i = 353$ mμ, $\lambda_u = 277$ mμ. ○, 3.93×10^{-5} *M*; ●, 4.68×10^{-6} *M*.

FIG. 2. The function log $(\Delta D_{BH^+} - \Delta D/\Delta D - \Delta D_B)$ plotted against $-H_0$ for 2,3;7,8-dibenzcyclooctadienone (XIII). ΔD, ΔD_{BH^+}, and ΔD_B are equal to $D_{353} - D_{277}$ in acid solutions in which XIII is partly ionized, completely ionized, and completely unionized, respectively.

Table I the basicities in terms of % H_2SO_4 in which the compounds are half ionized. Should it be found, in fact, that different scales are required for amine bases, carbonyl bases, etc., such an indication of a compound's basicity will still be meaningful.

Infrared Spectra of the Ketones

We have previously observed very good correlations between the basicities of substituted acetophenones and their carbonyl stretching frequencies (1). This is because the carbonyl stretching frequency and the basicity constant both tend to follow σ^+. However, when values for $\nu_{C=O}$ for diaryl ketones are plotted against both σ and σ^+ a roughly linear relation is obtained in each case. In fact, the correlation coefficients for the two lines are identical (0.978).* This probably reflects a somewhat diminished resonance effect between the carbonyl group and the para substituents in the benzophenones compared to both the acetophenone and the benzaldehyde conjugate acids, in agreement with the p*K* results.

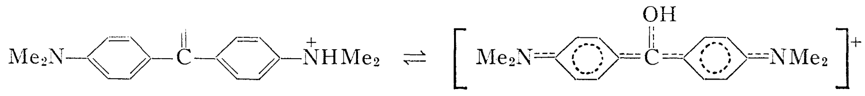
Ultraviolet Spectra of the Cations

A red shift (Δλ, Table I) of roughly 100 mμ in the ultraviolet maxima results from protonation of the carbonyl group, in most cases. This is about twice as large as the shift in the case of acetophenones and benzaldehydes (1). The effect of substituents on the absorption maximum of benzophenone conjugate acid is the same as on that of the diphenylmethyl cation, $(C_5H_6)_2CH^+$ (11). The derivatives of the latter carbonium ion each absorb at about 100 mμ longer wavelength than do the corresponding protonated benzophenone ions reported herein. However, there is a marked resemblance in the shape of the spectra of the isoelectronic ions $Ar_2\overset{+}{C}OH$ and $Ar_2\overset{+}{C}CH_3$ (12).

**When a parameter gives plots with the same degree of linearity (same correlation coefficient) with both σ and σ^+ this is usually reflected in a low value of the correlation coefficient. This is not always the case, however. A plot of σ against σ^+ for the following 14 groups,* p-NMe$_2$, p-NH$_2$, p-OH, p-OMe, p-C$_6$H$_5$, p-F, p-Cl, p-Br, m-F, m-I, m-Cl, m-CO$_2$Et, m-Br, m-CF$_3$, *using the data of Brown and Okamoto (8), gives an excellent linear relation (correlation coefficient, 0.998). It is obvious that no decision whatever could be reached about whether σ or σ^+ was being followed if one chose only substituents in this list.*

4,4′-Bis(dimethylamino)benzophenone

This compound protonates on nitrogen and the expected blue shift accompanies the formation of the doubly charged cation (348 to 251 mμ). The first and second protonation steps occur at approximately pH 3.0 and 1.2, respectively. We were interested in seeing if the presence of the resonance-stabilized cation XV, which should be in equilibrium with the ammonium monocation XIV, could be detected. By analogy with the behavior of the other benzophenones we would expect the carbonyl-protonated ion, XV, to absorb at about 500 mμ with an extinction coefficient in the range $3\text{–}5\times10^4$. The monocation produced in aqueous solution has no peak in the visible and, in fact, absorbs at about 380 mμ with an extinction coefficient somewhat smaller than that of the neutral compound. This is clearly the ammonium ion, XIV. Interestingly enough, in solvents such as acidified methanol and ethanol a small peak appears at 500 mμ and this is probably due to the ion XV. As the solution is made more acidic the intensity of this peak rises and then falls again as the ammonium dication is formed. Even in these solvents, however, only a small proportion, possibly 1%, of the monocation is in the form XV. Pfeiffer *et al.* (13) prepared the crystalline mono- and di-perchlorates of 4,4′-bis(dimethylamino)benzophenone; the diperchlorate is colorless but the monoperchlorate has a yellow cast and dissolves in ethanol and acetone to give a brown-red solution. The latter color is presumably due to the presence of the ion XV in the system.



XIV XV

Bridged Diaryl Ketones

The basicities of these compounds are listed in Table I. There are two effects, electronic and steric, which are clearly operative in this series. Fluorenone (IX) and dibenztropone (XII) each possess special electronic features which set them apart from the other ketones. Fluorenone is a derivative of cyclopentadienone and the well-known reluctance of that ring system to donate charge is reflected in fluorenone's low basicity; this, despite the increased conjugation of the aryl rings with the protonated carbonyl group which results from the rigid planar geometry of the molecule.

Dibenztropone (XII), on the other hand, possesses the highly basic tropone unit. The pK_{BH^+} value of -5.25 shows that this compound is more basic than its saturated analogue (XI), as expected, but it is clearly many powers of 10 weaker than tropone itself. This is in agreement with its known physical and chemical properties. Unlike tropone (14) it has a normal dipole moment, its carbonyl stretching frequency (1660 cm^{-1}) (15) is similar to that of benzophenone, and it forms a 2,4-dinitrophenylhydrazone. From this evidence it has been concluded that the molecule is folded (16).

Anthrone (X) is considerably more basic than benzophenone and this must be due chiefly to the increased conjugation between the protonated carbonyl group and the two rings. Although anthrone is not actually planar it is closer to this condition than is benzophenone (17, 18).

Increasing the number of carbons in the bridge forces the aromatic rings out of the plane of the carbonyl group and this causes the decrease in basicity observed in going from X to XI to XIII. The decrease due to steric factors would probably be greater than this were it not partly compensated by the increasing inductive effect of the alkyl substituents.

That is, the ortho substituent in the case of anthrone (X) is really a benzyl group containing a carbonyl substituent. In the case of dibenzcyclooctadienone (XIII) the ortho substituent is essentially alkyl in character.

It is worth noting that the effect of two ortho methyl groups in reducing the basicity of benzophenone by lowering the planarity of the system is considerably greater than the effect of a trimethylene bridge. Thus the $\mathrm{p}K_{\mathrm{BH}^+}$ value of 2,6-dimethylbenzophenone is -6.6 (7) compared to -6.2 for benzophenone and -5.8 for 2,3;7,8-dibenzcyclooctadienone (XIII).

EXPERIMENTAL

Reagents

The benzophenones which were commerically available reagents were crystallized several times to constant melting point as follows: benzophenone, 48–49°; 4-chlorobenzophenone, 75.5–76.5°; 4,4′-dimethylbenzophenone, 94–95°; 4,4′-dichlorobenzophenone, 148–149°; 4,4′-dimethoxybenzophenone, 144–145°; 4,4′-dihydroxybenzophenone, 210–212°; 4,4′-bis(dimethylamino)benzophenone, 174.5–175.5°; anthrone, 153–156°; fluorenone, 80–80.5°. 3,3′-Dininitrobenzophenone was prepared by the method of Barnett and Mathews (19). Nitration of diphenylmethane gave 4,4′-dinitrodiphenylmethane, which was oxidized with chromium trioxide to 4,4′-dinitrobenzophenone, m.p. 156–158°. 2,3;6,7-Dibenzsuberone was prepared from benzalphthalide (20) by the method of Cope and Fenton (21), b.p. 149–151° (0.3 mm). 2,3;6,7-Dibenztropone was prepared from the suberone by bromination with N-bromosuccinimide and subsequently dehydrobrominated with triethylamine (21), m.p. 88–89°. (All melting points are uncorrected.)

2,3;7,8-Dibenzcyclooctadienone

This compound was prepared from 2-(γ-phenylpropyl)benzoyl chloride (colorless oil, b.p. 153° at 0.65 mm, n_{D}^{20} 1.5812) by cyclization using the extreme dilution technique of Hedden and Brown (22). This procedure appears to be more successful than that used by Gutsche and co-workers (23).

To 7.5 g of aluminum chloride in 160 ml carbon disulphide was added, over a period of 10 hours, 6 g of 2-(γ-phenylpropyl)benzoyl chloride dissolved in 70 ml of carbon disulphide. The brown complex thus formed was decomposed on 200 g of crushed ice and became a cream-colored solid. The carbon disulphide was removed and the solid collected and dried in an Abderhalden pistol at 60°. The crude product was purified by sublimation (0.03 mm, 110°) followed by recrystallization from a 1:6 acetone – ethyl alcohol mixture. The colorless needles had m.p. 148–149°. Calc. for $C_{16}H_{14}O$: C, 86.46; H, 6.35. Found: C, 86.72; H, 6.65. (Thanks are due to Mr. D. Dolman for preliminary work on this preparation.)

2,4-Dinitrophenylhydrazone

The cyclooctadienone was kept for 3 weeks at 60° in a solution of 2,4-dinitrophenylhydrazine in diethyleneglycol containing a few drops of concentrated hydrochloric acid. The reaction mixture was then left for several weeks at room temperature. The crude product was recrystallized from glacial acetic acid. The obtained orange platelets turned yellow on grinding and had m.p. 195–196°. Calc. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51; N, 13.92. Found: C, 65.42; H, 4.50; N, 13.67.

Oxime

White needles, m.p. 146–148°. Calc. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.12; H, 6.37; N, 5.68.

Basicity Measurements

The p*K* measurements were made as previously described (1–4). In addition, since the absorption maxima of the neutral compounds and their conjugate acids were very far apart in most cases, a check was made by using absorption data at a single wavelength. Excellent agreement was obtained.

The ionization curve for 2,3;7,8-dibenzcyclooctadienone (XIII) using measurements at two different wavelengths is shown in Fig. 1. Low solubility of the neutral molecule required the use of two different substrate concentrations for the measurements. The logarithmic plot (3) should give a straight line of unit slope if the ionization behavior is normal. The slope of the line in Fig. 2 is close to unity, 0.94, with a correlation coefficient of 0.99.

The well-behaved character of both ionization plots in Figs. 1 and 2 may result from the fact that the absorption maxima of the neutral molecule and the cation are well separated. Tailing of the plots of $D_{\lambda\mathrm{i}} - D_{\lambda\mathrm{u}}$ against H_0 was not observed and it was not necessary to choose for $D_{\lambda\mathrm{u}}$ and $D_{\lambda\mathrm{i}}$ values which were 1.5 H_0 units away from the p*K*, as was done in a previous case (3).

In the case of the dinitro compounds the H_0 values of the solutions used were determined by indicator measurements. This is essential if one works with solutions whose H_0 value changes rapidly with concentration, since titration with base cannot hope to give sufficiently precise values of the acidity function.

ACKNOWLEDGMENT

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REFERENCES

1. R. Stewart and K. Yates. J. Am. Chem. Soc. **80**, 6355 (1958); Can. J. Chem. **37**, 664 (1959).
2. R. Stewart and K. Yates. J. Am. Chem. Soc. **82**, 4059 (1960).
3. R. Stewart and M. R. Granger. Can. J. Chem. **39**, 2508 (1961).
4. J. T. Edward, H. S. Chang, K. Yates, and R. Stewart. Can. J. Chem. **38**, 1518 (1960).
5. R. Stewart and L. J. Muenster. Chem. Ind. (London), 1906 (1961).
6. T. Handa and M. Kobayashi. Yoki Gosei Kagaka Kyoksai Shi, **13**, 580 (1955); Chem. Abstr. **51**, 8439 (1957).
7. A. Fischer, B. A. Grigor, J. Packer, and J. Vaughan. J. Am. Chem. Soc. **83**, 4208 (1961). D. S. Noyce and M. J. Jorgenson. J. Am. Chem. Soc. **84**, 4312 (1962).
8. H. C. Brown and Y. Okamoto. J. Am. Chem. Soc. **79**, 1913 (1957).
9. J. T. Edward and I. C. Wang. Can. J. Chem. **40**, 966 (1962). A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang. J. Am. Chem. Soc. **84**, 4343 (1962), and references therein.
10. R. W. Taft. J. Am. Chem. Soc. **82**, 2965 (1960). R. W. Taft and P. L. Levins. Anal. Chem. **34**, 436 (1962).
11. N. C. Deno, J. J. Jaruzelski, and A. Schriesheim. J. Am. Chem. Soc. **77**, 3044 (1955).
12. V. Gold and F. L. Tye. J. Chem. Soc. 2172 (1952).
13. P. Pfeiffer, K. Schwenzer, and K. Kumetat. J. Prakt. Chem. **143**, 143 (1935).
14. H. J. Dauben, Jr. and H. J. Ringold. J. Am. Chem. Soc. **73**, 876 (1951). W. von E. Doering and F. L. Detert. J. Am. Chem. Soc. **73**, 877 (1951).
15. E. D. Bergmann and D. Ginsburg. Bull. Res. Council Israel, **1**, No. 3, 120 (1951).
16. A. J. Birch. Ann. Repts., Chem. Soc. (London), **48**, 188 (1951).
17. R. N. Jones. J. Am. Chem. Soc. **67**, 2127 (1945).
18. R. Bramley and R. J. W. LeFevre. J. Chem. Soc. 56 (1962).
19. E. de B. Barnett and M. A. Mathews. J. Chem. Soc. **125**, 767 (1924).
20. R. Weiss. Organic syntheses. Coll. Vol. II. John Wiley and Sons Inc., New York. 1943. p. 61.
21. A. C. Cope and S. W. Fenton. J. Am. Chem. Soc. **73**, 1673 (1951).
22. G. D. Hedden and W. G. Brown. J. Am. Chem. Soc. **75**, 3744 (1953).
23. C. D. Gutsche, E. F. Jason, R. S. Coffey, and H. E. Johnson. J. Am. Chem. Soc. **80**, 5766 (1958).