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Intermediate Steps in Autoxidations

I. Enolization and Deuteration of Acetophenones in Acetic Acid

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Autoxidation of acetophenones in butyric acid solution is thought to proceed through the enol forms. Enolization of these compounds was therefore separately studied, employing acetic acid-*d* as a solvent. Rates of deuteration—presumed to be identical with rates of enolization—were determined by means of NMR analyses; the nuclear protons do not exchange and served as the internal standard for methyl protons. Substituent effects may be expressed in terms of a Hammett rho–sigma relationship, with $\rho = -0.7$ at 110°C and using the σ^+ constants proposed by Brown and Okamoto. For acetophenone, the Arrhenius activation energy (65–120°C) amounted to 16 kcal. The reactions were first order with respect to the ketones. Sodium acetate and pyridine showed a marked accelerating effect on H/D exchange rates, which was proportional to the amount of base. Base-catalyzed contributions to rate constants could be represented by a Hammett-type equation, with $\rho = +0.7$; however, σ constants led to a better fit than σ^+ substituent constants. Presumably, deuteration in the absence of base constitutes a true measure of enolization rates, i.e., it occurs through the enol, formed in a two-step process; base catalysis is attributable to reversible proton removal from the ketone.

INTRODUCTION

The present paper constitutes the first of a planned series on mechanisms of oxidation in organic solvents, in which various individual steps will be singled out and separately studied. In most of these processes homogeneous catalysis plays an important part.

In earlier papers (*1*) dealing with the autoxidation of isopropylbenzenes to benzoic acids in aliphatic acids as solvents (Mn catalyst), the assumption was made that enolization should be the rate-determining step. Among the supporting evidence was the fact that ketones containing a high proportion of the enolic isomer—such as α-benzoyl-α-methylacetone—reacted with Mn^{III} acetate at a high rate even at room temperature; after all the enol had been consumed, rates showed a sharp decline.

In this paper, we report on the enolization of acetophenones in acetic acid, followed by the determination of H/D exchange with the solvent. In Part II the results will be compared with those obtained in autoxidations carried out in the same solvents (*2*).

The basic assumption required when following enolization by means of side-chain deuteration, is that enol molecules, once formed, can only return to the ketone stage by taking up deuterium at the methylene group. Leading references as regards the course of enolization in aqueous media and its significance in halogenation, racemization, and deuteration are given by several authors, e.g., by Ingold (*3*), Reitz (*4*), Swain (*5*), and others (*6*). In many cases, enolization appears to be rate-determining, subsequent steps being much faster than the regeneration of the original ketone.

As for deuteration, it may be noted that this need not proceed (exclusively) through the enol form. Thus, as will be discussed later on, it may sometimes occur by a dif-

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ferent mechanism, such as reversible proton loss at the acyl group without the intermediacy of the enol.

Methods

In the present investigation, rates of deuteration were generally determined by reaction of acetophenones with a 30–35-fold excess of acetic acid-*d* (CH_3COOD) and following deuterium uptake. The best analytical method for this kinetic study appeared to be NMR. Since nuclear protons were found to undergo no exchange in the absence of strong mineral acids, peak heights for these protons ($\delta_{m,p-H}$ = 7.41 ppm; δ_{o-H} = 7.85 ppm; tetramethylsilane as standard) served as the internal standard for the acetyl protons (δ_{CH_3} = 2.50 ppm). This method had the additional advantage of requiring only small samples of material (100 mg). The large excess of deuterium source was necessary so as to avoid a too high dilution with protium at high conversions.

Using these methods, acetophenones as well as other acetyl compounds were studied at 110°C, including the effect of catalysts such as sodium acetate. For acetophenone, the effect of temperature was examined in the range 65–120°C.

Mass spectrometrical analyses (see Table 2) of partially deuterated acetophenone samples showed that the distribution of deuterium over the various deuterated compounds was the same as that calculated statistically on the basis of total deuterium content. Accordingly, it was assumed that no secondary isotope effects are obtaining within the limits of experimental accuracy, estimated to be about 5%. Thus, since the second deuterium atom is incorporated at the same rate as the first, etc., rate constants may be expressed by the equation

$$k_{(hr^{-1})} = -3(2.303/t_{(hr)}) \log (1 - x_t/x_\infty)$$

in which x_t and x_∞ represent the percentage of deuterium incorporated at times t and infinity. Plots based on this equation [log $(1 - x_t/x_\infty)$ vs. time] showed straight lines up to conversions of 50–75%; variations of ketone concentrations showed that deuteration occurs by a first order process.

Experimental

Materials

Starting materials were commercial samples or preparations by standard procedures. Physical constants closely agreed with literature values.

Acetic acid-*d* (*7*) was prepared by refluxing acetic anhydride with somewhat less than the theoretical amount of D_2O. The acetic acid-*d* thus obtained contained 95% deuterium in the OH group.

Acetophenone-ω-d_3 (*8*) was prepared by refluxing the ketone with an excess of D_2O in the presence of a small amount of potassium carbonate. This procedure was repeated three times. Mass spectrometrical analysis revealed a composition 97.5% d_3, 2.4% d_2, 0.1% d, 0.0% d_0.

Procedures

General

Deuterations were carried out on a microscale in a 25-ml reaction vessel equipped with a thermometer and a reflux condenser with $CaCl_2$ tube placed in a thermostat. Five milliliters of acetic acid-*d* (95% D; 90 mmole) was introduced. After the desired reaction temperature had been reached 3–4 mmole of the ketone was added. After suitable time intervals depending on the reaction temperature samples of 1 ml were taken by means of a syringe. To work up the reaction samples a rotating vacuum evaporator (Büchi, "Rotavapor") was used, equipped with an adapter which we designed for microdistillations (Fig. 1). This adapter, which is a double-walled mushroom-shaped extension piece of the rotator can be attached to it by a special glass ground joint. The outer space A is cooled by ice water. The acetic acid-*d*, which condenses on the cooled outer wall of B (= inner wall of A), runs by centrifugal force into the bottom of B, from which it can be collected by pouring it out of the adapter.

The residual acetic acid-*d* was stripped off in the same apparatus by distillation with carbon tetrachloride. The deuterium content of the residue was determined by NMR

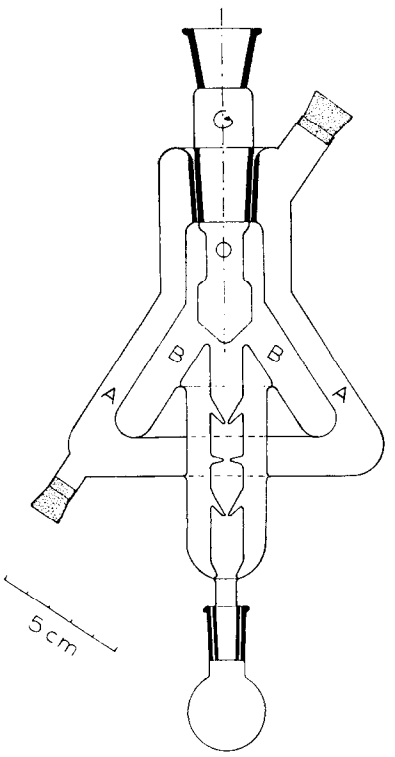


FIG. 1. Rotating collector attached to vacuum evaporator.

analysis. The percentages of deuterium incorporated were calculated using the formula

$$\%D = [1 - (nb/3a)] \times 100\%$$

in which b is the integrated NMR resonance signal of the acetyl protons; a, the integrated NMR resonance signal of the nuclear protons; and n is the number of nuclear protons—which do not exchange ($n = 5$, 4, 3, . . . for unsubstituted, mono-, disubstituted acetophenone, respectively). The NMR spectra were obtained with a Varian A60 NMR spectrometer operated at 60 Mc/sec. Solvents were CCl_4, $CDCl_3$, and CF_3COOH. Tetramethylsilane was used as reference standard.

Experiments in the presence of sodium acetate were carried out in the same manner, a known amount of the anhydrous acetate being added to the acetic acid-*d*. On working up the samples the sodium acetate was precipitated by adding carbon tetrachloride after distilling the acetic acid-*d*. The precipitate was filtered off and the filtrate worked up as described above. In the case of pyridine, removal of the latter appeared to be incomplete. However, the *ortho* hydrogens of this compound give a characteristic NMR signal at $\delta = 8.60$ ppm which does not overlap with other signals; accordingly, residual pyridine could be accounted for.

Examples

a. Deuteration of acetophenone. Table 1 gives the result of deuteration of acetophenone carried out at 90°C.

TABLE 1
DEUTERATION OF ACETOPHENONE IN ACETIC ACID-*d* AT 90°C (±0.5°C)[a]

Time (hr)	D incorporated (%)	k (hr^{-1})
1.5	10.0	0.220
3.0	16.8	0.202
4.5	23.5	0.197
6.0	30.7	0.204
7.5	37.2	0 208

[a] $k = -3/t \times 2.303 \times \log[1 - (\%D/92)]$; acetophenone: 0.56 mole/liter; acetic acid-*d*: 16.8 mole/liter; max. deviation in k: ± 7%; $k = 0.21$ h^{-1} (±4%).

b. Deuteration of *p*-methoxyacetophenone. At 110°C 703 mg of *p*-methoxyacetophenone (4.3 mmole) was dissolved in 10 ml of acetic acid-*d* (179 mmole). At intervals of 45 min samples of 2 ml were taken from the reaction mixture. After distillation of the acetic acid-*d* in a vacuum, the deuterium content was determined.

c. Deuteration of *p*-nitroacetophenone in the presence of sodium acetate. At 110°C 803 mg of *p*-nitroacetophenone (4.9 mmole) and 248 mg of sodium acetate (3.0 mmole) were dissolved in 10 ml of acetic acid-*d*. At time intervals of 30 min samples of 2 ml were taken from the reaction mixture. After removing the acid by distillation *in vacuo* the solid residue was dissolved in anhydrous chloroform. Sodium acetate was filtered off; chloroform was evaporated in a vacuum, the last traces being distilled with

carbon tetrachloride. Residues were then dissolved in $CDCl_3$, and analyzed by NMR.

d. Deuteration of 2-acetylfluorene. At 110°C 500 mg of 2-acetylfluorene (2.5 mmole) was dissolved in 10 ml of acetic acid-*d* (179 mmole). The reaction was carried out as described earlier. Solvent for the measurements was CCl_4. Calculation of the percentages of deuterium incorporated from NMR spectra was done using the formula

$$\%D = [1 - (7b/3a)] \times 100\%$$

with $n = 7$ (7 aromatic protons).

Mass Spectrometrical Analyses

These were carried out on a Consolidated C.E.C. 103-C instrument at an ionizing voltage of 70 eV. Results for samples of partially deuterated acetophenone are given in Table 2. The agreement between mass spectrometrical data and the deuterium distributions calculated statistically from the total amount of deuterium incorporated is very close, with the exception of the 3-hr run. Calculations show that secondary isotope effects exceeding 5% should cause marked deviations.

Occasional checks were also carried out on various other samples of deuterated acetophenone; these confirmed the NMR analysis.

TABLE 2
VARIATION OF DEUTERIUM DISTRIBUTION[a] WITH TIME

%	1 hr	2 hr	3 hr	4 hr	5 hr
d_0	55.0 (55.0)	31.5 (32.1)	16.9 (20.5)	11.3 (11.7)	7.8 (8.1)
d_1	36.7 (36.6)	45.1 (44.7)	49.9 (42.8)	36.8 (36.7)	31.9 (31.9)
d_2	7.8 (8.0)	20.5 (20.2)	26.8 (29.8)	39.0 (38.3)	42.6 (41.9)
d_3	0.5 (0.4)	2.9 (3.0)	6.4 (6.9)	12.9 (13.3)	17.8 (18.1)
Total %D	17.9	31.6	40.9	51.1	56.6[b]

[a] Acetophenone 0.58 mole/liter; CH_3COOD (95% D) 16.8 mole/liter, 110°C (±0.5°C). Figures in parentheses are the statistical values calculated on the basis of the total amount of deuterium incorporated.
[b] Total deuterium content as determined by NMR, 56%.

Occasional checks were also carried out on various other samples of deuterated acetophenone; these confirmed the NMR analysis.

RESULTS

a. Effect of temperature on deuteration of acetophenone in CH_3COOD. Table 3 presents the results of measurements in the range 65–120°C. The data lead to an Arrhenius energy of activation of 16 ± 0.5 kcal/mole.

TABLE 3
EFFECT OF TEMPERATURE ON RATE OF DEUTERATION OF ACETOPHENONE IN ACETIC ACID-*d* (95% CH_3COOD)[a]

Temperature (°C)	k (hr^{-1})
65	0.045
90	0.21
100	0.34
110	0.59
120	1.09

[a] Conc. acetophenone: 0.56 mole/liter; conc. acetic acid-*d*: 16.8 mole/liter. On the basis of duplicate runs, the maximum deviations in k values were less than 10%.

b. D–H exchange of acetophenone-ω-d_3 and CH_3COOH. Measurements made at 110°C showed that the rate constant is 0.22 (hr^{-1}) as compared with 0.59 for the

TABLE 4
DEUTERIUM CONTENT OF ACETIC ACID-*d* VS. DEUTERATION RATES (110°C)[a]

%D	k (hr^{-1})	k/%D
28.0	0.09	0.32
49.5	0.18	0.36
70.0	0.30	0.43
87.6	0.50	0.57
95.0	0.59	0.62
100	0.66[b]	0.66[b]

[a] Conc. acetophenone: 0.56 mole/liter; conc. acetic acid-*d*: 16.8 mole/liter; max. deviation in k: 5–10%.
[b] Extrapolated values.

reaction acetophenone–CH_3COOD. The implications of this significant isotope effect will be discussed further on as well as in Part II.

c. Effect of deuterium content in acetic acid-*d* on rates of deuteration of acetophenone. The data given in Table 4 indicate that the dilution effect is far from linear, presumably because both a "solvent isotope effect" and a "direct isotope effect" are involved (cf. Sec. b).

d. Effects of sodium acetate and of pyridine. These basic compounds were found to accelerate rates of deuteration of acetophenone. Rate constants can be simply expressed in the form

$$k_{\text{exptl}} = k_0 + k_B[B]$$

in which [B] equals the concentration of added sodium acetate and k_0 is the rate constant in the absence of base B. With pyridine, the effects were less pronounced (cf. Table 5). Other acetophenones showed the same behavior (see Sec. e).

TABLE 5
EFFECTS OF NaOAc AND OF PYRIDINE ON DEUTERATION RATES OF ACETOPHENONE IN ACETIC ACID-*d* AT 110°C[a]

B	[B] (mole/liter)	[Acetophenone] (mole/liter)	k_{exptl} (hr^{-1})	k_B ($mole^{-1}$ liter $hour^{-1}$)
Sodium acetate	0.16	0.56	1.22	3.88
Sodium acetate	0.28	0.56	1.68	3.86
Sodium acetate	0.28	0.56[b]	0.70[b]	1.55[b]
Pyridine	0.57	0.56	1.73	2.02

[a] [Acetic acid-*d*]: 16.8 mole/liter; max. deviation in *k*: 5–10%.

[b] Experiment with acetophenone-ω-d_3 in acetic acid-*h*.

e. Substituent effects on deuteration. Electron-withdrawing substituents retard deuteration whereas electron-donating groups cause higher rates (Table 6). Conjugative effects are also important, as is demonstrated in Table 7. The influence of added sodium acetate on the deuteration of substituted acetophenones is recorded in Table 8. It appeared to be the stronger, the more pronounced the electron-withdrawing effect of the substituent; in fact, at the concentration of sodium acetate employed the latter compounds were found to be even more reactive than the unsubstituted ketone.

TABLE 6
m- AND *p*-SUBSTITUENT EFFECTS[a] ON THE DEUTERATION OF ACETOPHENONES (110°C)[b]

S	k (hr^{-1})	$\log k_S/k_H$	σ^+	σ
p-$(CH_3)_2N$	5.00	0.930	−1.43	−0.600
p-CH_3O	1.52	0.410	−0.764	−0.268
p-CH_3	1.02	0.236	−0.302	−0.170
p-C_6H_5	0.84	0.159	−0.179	−0.009
H	0.59	0	—	—
p-Br	0.44	−0.142	0.148	0.238
m-Br	0.32	−0.270	0.391	0.391
p-COOH	0.31	−0.274	0.390	0.390
4-CH_3CO	0.29	−0.308	0.501	0.501
p-CN	0.30	−0.290	0.628	0.628
m-NO_2	0.28	−0.330	0.662	0.710
p-NO_2	0.26	−0.356	0.778	0.778
3,5-di-Cl	0.23	−0.412	0.746	0.746
3,5-di-Br	0.24	−0.370	0.782	0.782
3,5-di-CH_3CO	0.23	−0.412	0.612	0.612
3-NO_2,4-Cl	0.21	−0.445	0.832	0.937
3,5-di-NO_2	0.11	−0.720	1.324	1.420

[a] See Ref. 13.

[b] [X—C_6H_5—$COCH_3$]: ~0.5 mole/liter; [CH_3COOD]: 16.8 mole/liter; max. deviation in *k*: ~10%.

TABLE 7
DEUTERATION OF ACETYL DERIVATIVES OTHER THAN ACETOPHENONES (110°C)[a]

R-	k (hr^{-1})
2-Naphtyl	0.74
3-Phenanthryl	0.96
2-Fluorenyl	1.74
2-Thienyl	0.48
2-Pyridyl	9.80
4-Pyridyl	4.17
(Phenyl-)	0.59
(Phenyl-)[b]	1.73[b]

[a] [R—CO—CH_3]: ~0.5 mole/liter; [CH_3COOD]: 16.8 mole/liter; max. deviation in *k*: ~10%.

[b] In the presence of an equimolecular amount of pyridine.

TABLE 8
DEUTERATION RATES OF SUBSTITUTED ACETOPHENONES IN CH_3COOD IN THE PRESENCE OF NaOAc AT 110°C[a]

S	k_{expt} (hr^{-1})	NaOAc (mole/liter)	k_0 without NaOAc (hr^{-1})[b]	k_B ($mole^{-1}$ liter hr^{-1})
p-CH_3O	2.02	0.23	1.52	2.18
p-CH_3	1.71	0.28	1.02	2.50
H	1.68	0.28	0.59	3.86
p-Br	1.84	0.28	0.44	5.00
p-NO_2	4.11	0.28	0.26	13.70

[a] [X—C_6H_5—$COCH_3$]: ~0.5 mole/liter; [CH_3-COOD]: 16.8 mole/liter; max. deviation in k: ~10%.

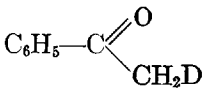
[b] First order rate constant. See Table 6.

DISCUSSION

General

The kinetics and mechanisms of enolization have mostly been studied in aqueous systems. In the presence of base, enol anions rather than enols are formed, whereas the enols are true intermediates in more or less acidic systems.

In view of the extremely low ion concentrations in acetic acid (autoprotolysis constant 3.5×10^{-15} at 25°C) (*9*), the more or less generally accepted Pedersen scheme (*10*, *11*) seems unlikely to hold for glacial acetic acid also. This scheme involves reversible protonation at the carbonyl oxygen as the primary step, followed by proton loss at the α-carbon atom. However, a closely analogous scheme (Fig. 2) can be written in which complex formation with acetic acid is the primary step, followed by proton loss ("rearrangement"), in a fashion similar to that proposed by Swain (*11*) for the mutarotation of glucose. The reverse of (2), with CH_3COOD, then leads to



This scheme is supported by the detection (*12*) of a similar complex formation in acetone–acetic acid mixtures. It leads to the following rate equation:

$$-\ln [1 - ({}^{x}t/x_{\infty})] = k_1k_2/(k_{-1} + k_2)t_1[CH_3COOD]$$

in which x_t and x_∞ represent the percentages of deuterium incorporated at times t and infinity. Thus, the experimental rate constant k becomes $k_1k_2/(k_{-1} + k_2)$.

For $k_2 \gg k_{-1}$, this reduces to k_1; deuteration is determined by the rate of complex formation. For $k_2 \ll k_{-1}$, the experimental rate constant becomes equal to the equilibrium constant for complex formation (k_1/k_{-1}) multiplied by k_2. In the former case, one should not expect a large difference between the rate of deuteration of acetophenone and that of deuterium removal from acetophenone-ω-d_3. According to the above scheme, important isotope effects could

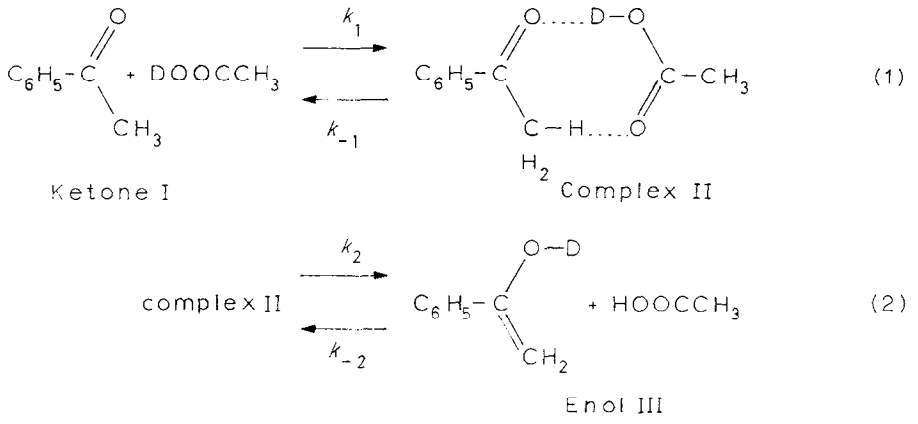


FIG. 2. Suggested mechanism of enolization and deuteration of acetophenone in CH_3COOD.

only arise from differences with respect to k_2, the rate constant for a reaction involving C–H bond breaking. As will be shown in Part II of this series, on the basis of autoxidation runs, the solvent isotope effect (i.e., that due to the change from CH_3COOD to CH_3COOH) is leading to a small *increase* of reactivity when going from CH_3COOD to CH_3COOH.

The Arrhenius activation energy (16 kcal) for deuterations of acetophenone in the range 65–120°C is of the same order of magnitude as that for halogenations of acetophenone in aqueous acetic acid, which is reported to be about 20 kcal (*13*).

Effect of Deuterium Content of the Acetic Acid on Rates of Deuteration

Table 4 indicates that the dilution effect is nonlinear. Presumably, the light solvent is somewhat more strongly acidic than the deuterated acid; regeneration of ketone from the enol form by the light acid should then be faster than that by the heavy solvent. This agrees with Reitz' findings for acid-catalyzed brominations of acetophenone being 20% faster in H_2O compared with D_2O (*4*). The value at 100% deuterium content obtained by extrapolation (Table 4) should be equal to the rate of enolization and will be used for comparison with autoxidation rates in Part II.

Base Catalysis and Substituent Effects in the Deuteration of Acetophenones

The accelerating effect of added sodium acetate or pyridine could be due either to catalysis of enolization (e.g., proton removal from the ketone-acid complex) or to a direct proton removal from the *free* ketone; in the latter case, deuteration proceeds via the enol (= ketone) anion. The latter possibility

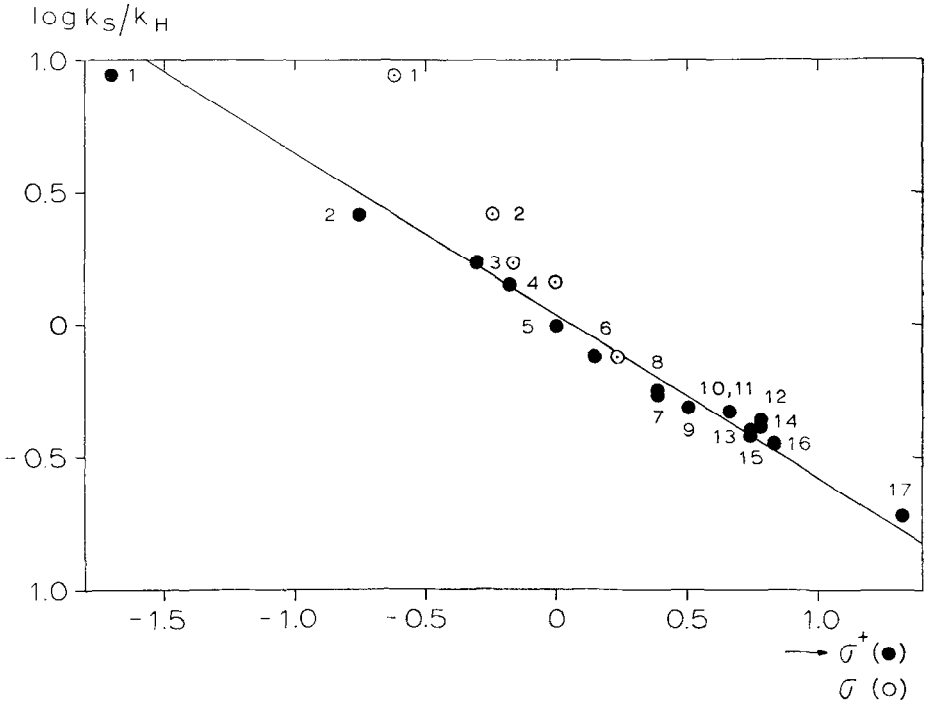


FIG. 3. Log k_S/k_H for deuteration of some substituted acetophenones at 110°C vs. σ and σ^+ constants (○ and ●, respectively). The numbers refer to the following substituents: 1: *p*-$N(CH_3)$; 2: *p*-OCH_3; 3: *p*-CH_3; 4: *p*-C_6H_5; 5: H; 6: *p*-Br; 7: *m*-Br; 8: *p*-COOH; 9: *p*-$COCH_3$; 10: *p*-CN; 11: *m*-NO_2; 12: *p*-NO_2; 13: 3,5-di-Cl; 14: 3,5-di-Br; 15: 3,5-di-$COCH_3$; 16: 3-NO_2, 4-Cl; 17: 3,5-di-NO_2. Sigma constants for disubstituted acetophenones were obtained by addition of the individual values, which were taken from H. H. Jaffe, *Chem. Revs.* **53**, 191 (1953), and from Brown and Okamoto, *J. Am. Chem. Soc.* **80**, 4979 (1958), for σ and σ^+, respectively.

seems more plausible, as will be discussed below.

Substituent effects on deuteration appear to obey a Hammett rho–sigma relationship, σ^+ values due to Brown and Okamoto (*14*) showing an appreciably better fit than the classical σ constants (Fig. 3).

That σ^+ constants are to be preferred is also demonstrated by the results obtained with other acetyl compounds, which are plotted in Fig. 4. It may be noted that

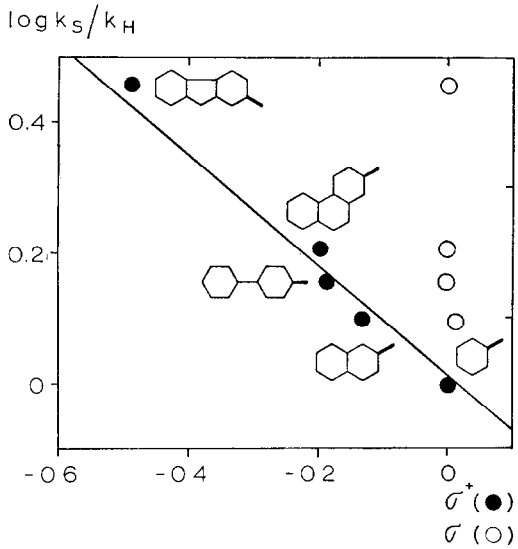


FIG. 4. Log k_R/k_H for deuteration of some aromatic acetyl compounds in acetic acid-*d* at 110°C vs. σ and σ^+ (○ and ●, respectively).

Stewart and Yates (*15*) found a σ^+ correlation for the pK_a values of substituted acetophenones in strong mineral acid.

Although a fairly satisfactory straight line was obtained, it is not obvious why the rho value observed is -0.9 rather than -0.7 as in the plot given in Fig. 3. However, both graphs clearly illustrate the importance of resonance stabilization of a positively charged species.

Figure 5 presents a plot of log k_{exptl} for some *p*-substituted acetophenones in the presence or absence of the same amount of sodium acetate against σ^+.

At the concentration of sodium acetate employed, the *p*-nitro derivative appears to be even markedly *more* reactive than the unsubstituted compound. This seems to be difficult to reconcile with the assumption that the base simply facilitates proton removal from the complex; it would mean that this proton removal should be more strongly affected by a substituent than that by acetic acid (or acetate ion, step 2). On this basis, it seems more plausible to assume that deuteration is accelerated by a contribution from the ionization process mentioned in the first paragraph of this discussion. This alternative has been also postulated by Watson *et al.* to account for their results on the acetate catalyzed halogenation of acetophenones (*16*). It is further supported by the substituent effects applying to the "catalyzed portions" of the total rates in the presence of the same amount of sodium acetate. As mentioned earlier, these total rates may be expressed as $k_0 + k_B[B]$ in which k_0 refers to the uncatalyzed process. Figure 6 presents a plot of log $(k_S/k_H)_B$ against σ and σ^+.

The admittedly limited number of experimental points suggests that, in this case, σ constants are providing a better fit than σ^+ constants. Since proton removal from a positively charged species should be subject to "σ^+ effects" rather than "σ effects," this argues against the latter mechanism and favors proton removal from the uncharged ketone. The value of rho based on σ values amounts to 0.72. It may be noted that, since no conjugation can occur between the $COCH_2^-$ group and substituents, the σ constant for *p*-nitro ($+0.78$) should be used rather than the σ^- value ($\sim +1.1$) applying to its effect on the acidity of phenols and anilinium ions. As for the effects of various nuclei on acetyl derivatives, the high reactivity of the acetyl pyridines is noteworthy. Here, the pyridine bases may act as basic catalysts; this effect should be especially pronounced because of the electron-withdrawing properties of the aza substituent. The acidic properties of side-chain hydrogens in nitrotoluenes (*17*) and methylpyridines (*18*) causing H/D exchange are well established. The very high deuteration rate observed with 2-acetylpyridine could be due to a concerted process in which the nitrogen atom acts as the proton-removing species, either directly or with the aid of a molecule of acetic acid.

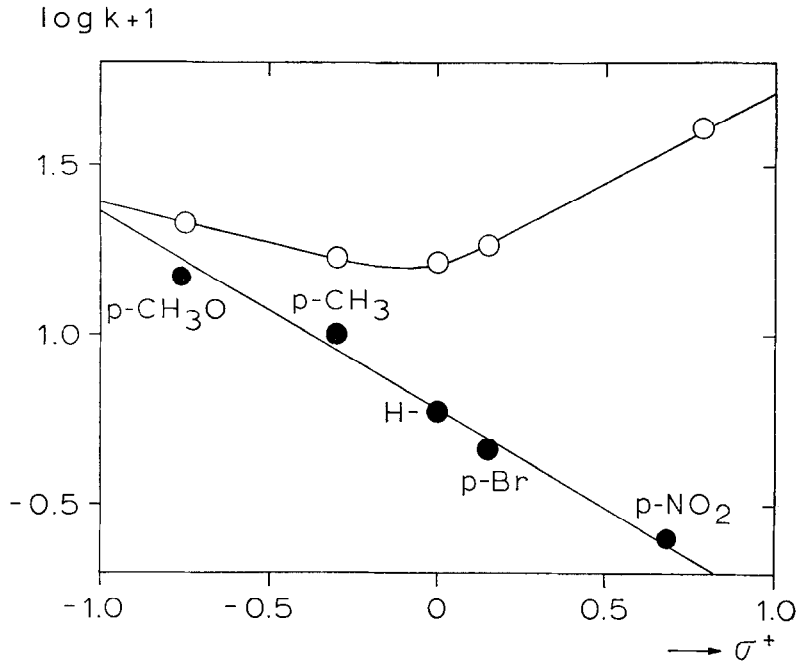


FIG. 5. Log k_{exptl} for deuteration of some *p*-substituted acetophenones in the presence (○) or absence (●) of 0.28 mole/liter of sodium acetate (110°C) vs. σ^+.

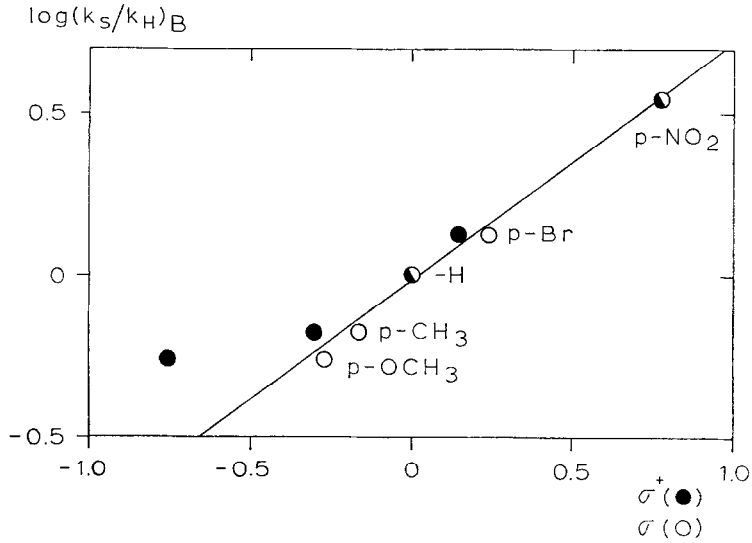


FIG. 6. Log $(k_S/k_H)_B$ for deuteration of substituted acetophenones in acetic acid in the presence of 0.28 molar sodium acetate at 110°C vs. σ and σ^+.

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