tendency to form 2:1 adducts. (Note: This presumably is a result of cycloreversion and not product formation directly from III.) Qualitatively the product formation is considerably slower (in 15 h, 10% by NMR) than from I and DMAD directly.

The Sensitized Irradiation of I and DMAD in Methanol-*O*-*d*. Six samples each containing 100, 50, and 25 mg of DMAD, I, and acetophenone, respectively, in 6 mL of CH_3OD solution are irradiated for 36 h. The solvent is removed at reduced pressure with a hot water bath. Preparative TLC is used to isolate III. Further purification is carried out by preparative GC, followed by mass spectral analysis of the isolated product. Comparison with an authentic sample of IV shows that the IV obtained in methanol-*O*-*d* is a mixture of IV-d_0 (41%) and IV-d_1 (59%).

Variable-Temperature ^{1}H NMR. The variable-high-temperature ^{1}H NMR experiments on compounds IX and VII are carried out on a Varian CFT-20 spectrometer equipped with a variable temperature controller (Varian V6040 controller) and using Me_2SO-d_6 as solvent. The temperature calibrations are made by using an ethylene glycol standard and are performed at each temperature studied. The solvent used is a 50:50 $CDCl_3$ Me_2SO-d_6 mixture. At the lowest temperatures (cooled in dry ice–acetone and warmed in probe) observed $\Delta\nu$ is constant for VIII at 11.0 Hz.

The free energies of activation are determined by using eq 10 and 11. The values of $\Delta\nu$ are determined from the "low" temperature spectra. The values of $\Delta\nu$ are, for VIII, 11 Hz (J = 0 Hz) at δ 1.94 and, for VII, 4.4 Hz (J = 0 Hz) at δ 2.23 and 10.6 Hz (J = 7.0 Hz) at δ 0.91. The coalescence temperature, T_c, for VIII at δ 1.97 (45 °C) is determined directly, while the T_c's for VII at δ 0.91 and δ 2.23 are extrapolated to 200 and 220 °C, respectively. The free energies of activation, $\Delta G^{\ddagger}$, obtained are 16.6 kcal/mol for VIII and 26.2 and 26.0 kcal/mol for VII.

$$k_c = (\Delta\nu^2 + 6J^2)^{1/2}/2 \quad (10)$$

$$\Delta G^{\ddagger} = RT_c\,(\ln (R/Nh) + \ln (T_c/k_c)) \quad (11)$$

Acknowledgment. This work was supported by the National Institutes of Health (1 RO1 NS 14883-01). It was taken, in part, from the Ph.D. thesis of Paul D. Davis, submitted to the Graduate School of the University of Toledo. Helpful discussions with Dr. Roger Card and Professor J. C. Dalton are hereby acknowledged.

Registry No. I, 875-30-9; I-d_3, 72206-02-1; I-*d*, 72206-03-2; II, 34187-47-8; III, 69496-51-1; IV, 34203-07-1; V, 34219-44-8; VII, 72206-04-3; VII-d_2, 72206-05-4; VII-d_6, 72214-05-2; VIIa, 72206-06-5; VIII, 72206-07-6; VIII-d_6, 72206-08-7; IX, 72206-09-8; IX-d_6, 72206-10-1; DMAD, 762-42-5; 3-*tert*-butyl-1-methylindole, 46270-99-9; 1-methyl-3-phenylindole, 30020-98-5; 1-methylindole, 603-76-9; i, 72206-11-2; ii, 72206-12-3; iii, 72206-13-4.

Stability of Carbon-Bonded Anionic σ Complexes. 3.[1,2] Decomposition in Aqueous Acidic Media

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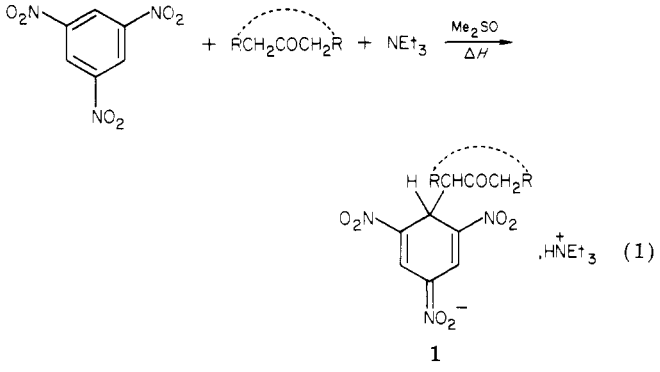
Kinetic data for the acid-catalyzed and uncatalyzed decomposition of anionic σ complexes of 1,3,5-trinitrobenzene and simple ketones are discussed. The ^{13}C NMR spectral characteristics of certain complexes are presented, and chemical shifts of the carbonyl carbon in the complexes are correlated with structure and rates of decomposition in aqueous media.

For some time we have been interested in the factors which contribute to the stability, in aqueous media, of anionic σ complexes (Meisenheimer complexes) formed from simple enolates and *sym*-trinitrobenzene (TNB). We have previously reported relative thermodynamic heats of formation for a series of such complexes formed from simple acyclic and cyclic ketones in Me_2SO, initiated by triethylamine (eq 1).[1,2] These relative heats of formation do not provide a direct measure of complex stability but do allow comparisons which are of interest. For example, the very large heat of formation found for the cyclopentanone complex provided a qualitative rationale for its unusual stability, even in 0.1 M acid. We have previously commented on possible explanations for this large heat of formation.[2]



(1)

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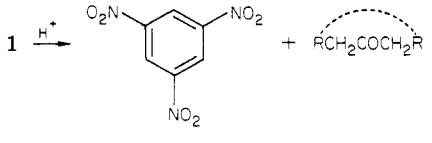
We report here kinetic data for the decomposition of complexes like 1 in acidic solution from pH 0 to pH 6. The complexes were prepared from acetone, diethyl ketone, cyclopentanone, cyclohexanone, cycloheptanone, acetophenone, *p*-methoxyacetophenone, *p*-cyanoacetophenone, and *p*-nitroacetophenone. These kinetic data, especially those obtained for the para-substituted acetophenones, allow characterization of the mechanism of decomposition (eq 2) in more detail than has previously been possible.



(2)

Methods of Procedure

The complexes were all prepared, with minor variations (see Experimental Section), by dissolving 1 equiv of TNB

(1) M. J. Strauss, R. M. Murphy, and C. A. Wulff, *J. Am. Chem. Soc.*, **96**, 2678 (1974).
(2) C. A. Wulff, R. M. Murphy, and M. J. Strauss, *J. Org. Chem.*, **40**, 1499 (1975).

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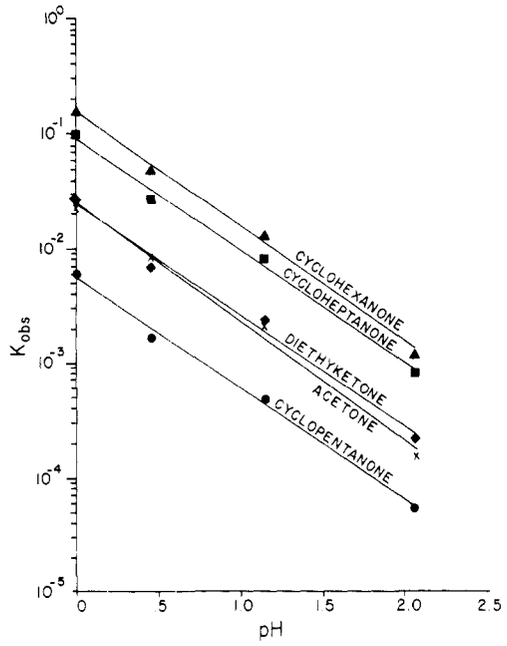


Figure 1. pH–rate profile for the decomposition of simple alicyclic and cyclic ketone σ complexes of TNB at 30 °C.

in excess ketone and adding a fourfold equivalent excess of triethylamine as described previously.[1] After the complexes crystallized from the reaction mixture, they were filtered off, washed with copious amounts of anhydrous ether, and vacuum dried for at least 24 h. They all exhibited similar electronic spectra in the visible region with maxima at ~450 and ~550 nm (in methanol).[3]

To obtain a rate constant for decomposition in aqueous solution, we dissolved the complex in Me_2SO (~20 mg/mL), and approximately 5 μL of this solution was injected directly into a thermostated cuvette containing the appropriate buffer or HCl solution. The ionic strength of these solutions was 1.0 and the pH was measured directly in the cuvette before injection. Immediately after injection of the Me_2SO solution of the complex, the stoppered cuvette was vigorously shaken and placed in the thermostated spectrophotometer, and the decrease in absorbance at 470 nm was measured as a function of time. Two or three runs were made for a single complex at any pH. The rate constants were obtained by the Guggenheim method,[4] and the error between runs did not exceed 5%. The rates of decomposition of the simple acyclic and cyclic ketones were quite low, and these were obtained only at very low pH (Figure 1). The rates of decomposition of the acetophenone complexes as a function of pH are summarized in Figure 2.

Results and Discussion

It is apparent that a hydrogen-ion-catalyzed decomposition of these complexes occurs in the low-pH region as evidenced by the approximate tenfold increase in k_{obsd} between pH ~1 and pH ~2 (Figures 1 and 2). At higher pH it was extremely difficult to accurately measure rates for the simple acyclic and cyclic ketones as these are remarkably stable in this region. In contrast, we were able to measure the rates of decomposition of the para-substituted acetophenone complexes throughout the range from pH 1 to pH 6. These pH–rate profiles (Figure 2) exhibit two regions corresponding to the acid-catalyzed decomposition (pH 1–2) and the uncatalyzed decomposition (pH 5–6). This can be expressed in the form of a rate law for decomposition where k_a and k_o are the rate constants for the catalyzed and uncatalyzed processes, respectively (eq 3). For the simple acyclic and cyclic ketones

$$-d[1]/dt = k_a[H_3O^+][1] + k_o[1] \quad (3)$$

$$k_{obsd} = k_a[H_3O^+] + k_o \quad (4)$$

above pH ~3.0, the term $k_a[H_3O^+]$ is very small, and k_o is not sufficiently large for the overall rate to be measured accurately. For the acetophenone complexes the two terms are of similar magnitude at pH ~3, and the k_o term only becomes predominant above pH 4. This allows determination of absolute values of k_o in this region for each acetophenone complex (vide infra). These constants are clearly much larger than the k_o values for complexes of the simple acyclic and cyclic ketones. This is not unexpected since forming enolate in the decomposing acetophenone complexes is conjugated.

For the acetophenone complexes, values of k_a are obtained by plotting k_{obsd} vs. $[H_3O^+]$ (eq 4; k_a = slope). Values of k_o are obtained from the region above pH 4.0 where the $k_a[H_3O^+]$ term is negligible. These rate constants are summarized in Table I. The lines drawn in Figure 2 were obtained by using values of k_a and k_o (Table I) and calculating k_{obsd} at various hydrogen ion concentrations, and they fit the experimental points very well. The slopes of the curves in the acidic region (pH 0–1.5) are 1.0 for the *p*-MeO and *p*-H complexes where $k_a[H_3O^+] \gg k_o$. For the *p*-NO_2 and *p*-CN complexes the slopes are significantly less than 1.0 (0.83 and 0.93, respectively) because *the contribution of k_o to k_{obsd} is still significant in this region*; i.e., for the *p*-NO_2 complex at pH 1, k_o is ~10% of k_{obsd}. The large rate of uncatalyzed decomposition for the complexes with electron-withdrawing substituents (eq 5) is understandable since the X substituent stabilizes the forming enolate to varying degrees and is thus an intrinsic factor controlling the magnitude of k_o, i.e.,

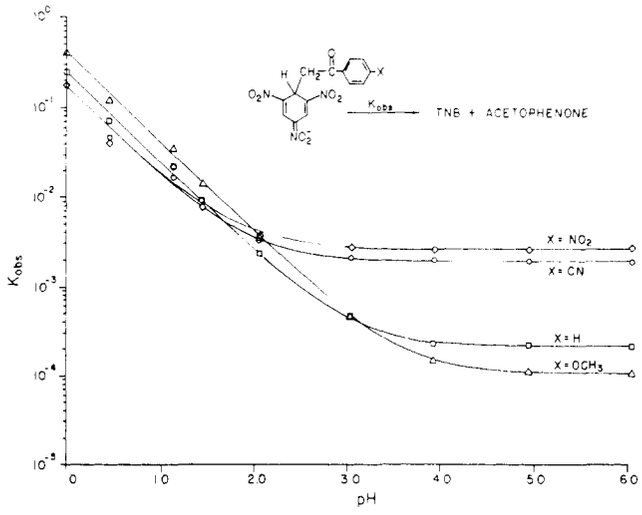
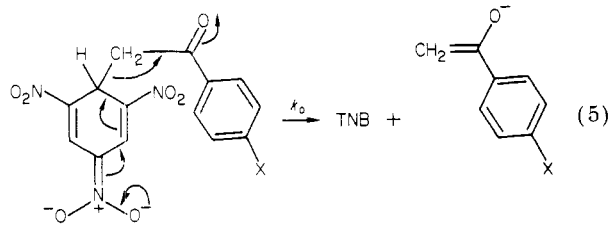


Figure 2. pH–rate profile for the decomposition of para-substituted acetophenone σ complexes of TNB at 30 °C.

Table I. Rates of Decomposition of Para-Substituted Acetophenone Complexes of TNB

substnt	k_a, M^{-1} s^{-1}	log k_a	$10^4 k_o$, s^{-1}	log k_o	σ
OMe	0.43	−0.36	1.08	−3.97	0.27
H	0.25	−0.60	2.27	−3.64	0
CN	0.17	−0.77	19.50	−2.71	+0.63
NO_2	0.17	−0.77	26.60	−2.575	+0.78

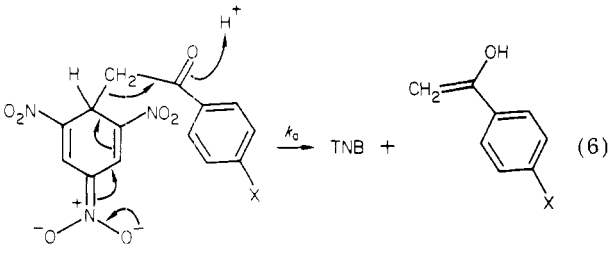
(3) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).
(4) E. A. Guggenheim, *Philos. Mag.*, **2**, 538 (1926).



(5)

$k_o(NO_2) \gg k_o(OCH_3)$. A plot of log k_o vs. the σ_p values of the acetophenone para substitutents is shown in Figure 3. The slope of this line, ρ for the decomposition, is +1.4. This is indicative of significant negative charge development at the carbonyl carbon in the complex during carbon–carbon bond cleavage.

In the more acidic region where H^+ catalysis is occurring, protonation yields an enol which is *not* significantly stabilized by the para ring substituent (eq 6). The values

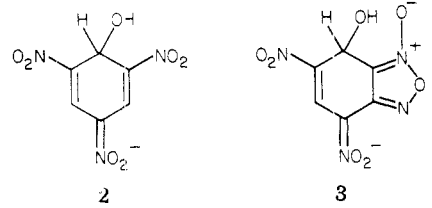


(6)

of k_a are therefore similar for all the acetophenone complexes. In fact, in the low-pH region the acetophenone and methoxyacetophenone complexes react *faster* than their *p*-nitro and *p*-cyano analogues. This is illustrated quantitatively by a plot of log k_a vs. σ (Figure 3) which provides a ρ of −0.33. This indicates that the extent of oxygen–hydrogen bond formation is equal to or *exceeds* that of carbon–carbon bond breaking in the transition state for the acid-catalyzed process.

The *p*-nitroacetophenone complex, with the highest k_o value of all the complexes studied (k_o = 0.0027 s^{-1}), decomposes spontaneously 4 × 10^3-fold *more slowly* than **2**[5] (k_o = 9.8 s^{-1}). This is because the formation of enolate requires both carbon–carbon bond cleavage and concomitant rehybridization from sp^3 to sp^2, as well as substantial solvent reorganization. These are the same phenomena responsible for the well-known very low rates of carbon-acid deprotonation and enolate protonation.[6]

The k_a for acid-catalyzed decomposition of **2** is not known. However, the acid-catalyzed decomposition of **3**, which is 10^{10}-fold more stable than **2**, has a k_a of 146 M^{-1}



2 3

s^{-1}.[7] This is much larger than k_a values for the acetophenone complexes which, in turn, have k_a values larger than those of the simple acyclic and cyclic ketones. Two factors contribute importantly to these large rate differences. Clearly the protonated hydroxyl in the acid-catalyzed decomposition of **2** or **3** is a much better leaving group than the protonated ketone moiety in **1**, since the positive charge promoting bond cleavage is directly on the departing atom in **2** and **3**. This charge is two atoms removed in **1**. The other factors responsible for these large differences are the hybridizational changes and solvent reorganization occurring during decomposition of **1**, an effect also responsible for large differences in k_o in going from **1** to **2** or **3**.

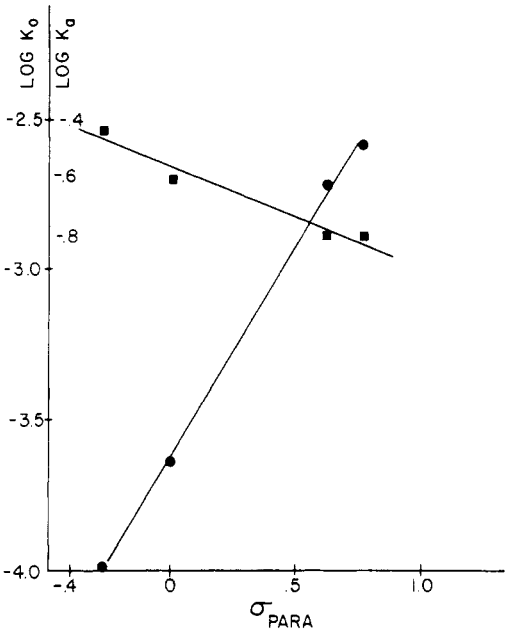
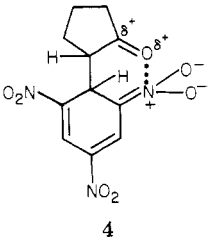


Figure 3. Hammett plots for the catalyzed (k_a) and uncatalyzed (k_o) decompositions of acetophenone σ complexes of TNB.

The pH–rate profiles for the complexes of acetone, diethyl ketone, cyclopentanone, cyclohexanone, and cycloheptanone (Figure 1) show distinct differences in acid-catalyzed decomposition rates. The values of k_a are summarized in Table II, along with selected C-13 shifts of the complexes and parent ketones. While all these decompositions show clear first-order hydrogen-ion-catalyzed decomposition, the rate for the cyclopentanone complex is unusually low. This is in accord with the previously reported very large heat of formation.[1,2] This complex is so unreactive that its half-life in 1 M acid is ~2 min. This unusual stability has previously been accounted for by a proposed conformation of the complex (observed with Dreiding models) in which the carbonyl oxygen is favorably located for a stabilizing interaction with the positively polarized nitrogen of an adjacent nitro group.[1] This interaction is supported by two characteristics of the ^{13}C NMR spectrum of the complex. First, the unusually low field position of the carbonyl carbon in the complex, relative to all the other complexes, supports a highly polarized C=O function, as suggested by the proposed conformation (**4**). Second, the barrier to rotation about the cyclo-



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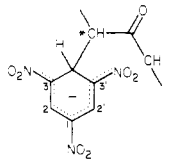
hexadienate–cyclopentanone bond, enhanced by the proposed interaction, is reflected in a greater nonequivalency of the C-3 cyclohexadienate ring carbons than in any of

(5) C. F. Bernasconi, *J. Am. Chem. Soc.*, **92**, 4682 (1970).
(6) (a) J. R. Jones, "The Ionization of Carbon Acids", Academic Press, London, 1973. (b) E. Buncel, "Carbanions: Mechanistic and Isotopic Aspects", Elsevier, Amsterdam, 1975.
(7) F. Terrier, F. Millot, and W. P. Norris, *J. Am. Chem. Soc.*, **98**, 5883 (1976).

Table II. Selected ^{13}C Chemical Shifts and Rates of Acid-Catalyzed Decomposition of Alicyclic and Cyclic Ketone Complexes of TNB



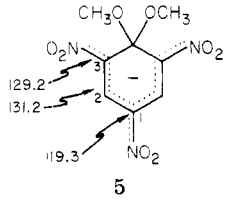
	k_a, M^{-1} s^{-1}	k_{rel}	parent ketone δ_{CO}	δ_{CO}	$\Delta\delta_{CO}$	δ_{C-1}	$\delta_{C-2,2'}$	$\Delta\delta_{C-2,2'}$	$\delta_{C-3,3'}$	$\Delta\delta_{C-3,3'}$
cyclopentanone	0.0057	1	213.9	214.3	+0.4	121.0	126.8 128.0	1.2	131.4 134.2	2.8
diethyl ketone	0.025	4	209.3	209.2	−0.1	121.4	128.0 128.4	0.4	129.8 132.0	2.2
acetone	0.026	5	205.1	205.1	0	121.2	127.3	0	132.9	0
cycloheptanone	0.093	16	211.7	211.3	−0.4	121.6	127.6 128.3	0.7	130.3 132.4	2.1
cyclohexanone	0.160	28	208.8	207.0	−0.8	121.3	126.7 127.6	0.9	131.3 133.4	2.1

the other asymmetric complexes (i.e., those of cyclohexanone, cycloheptanone, and diethyl ketone). This latter phenomenon was previously observed in the proton spectra of the complexes,[8] but the effect in the carbon spectra is much more profound (Table II) and will now be discussed briefly.

The ^{13}C NMR shifts for carbons on the trinitrocyclohexadienate portion of the complexes provide information about the structure and charge distribution in these anions. The chemical shift of the C-1 para nitronate carbon for *all* the complexes is 121.43 ± 0.20 ppm, except for the cyclopentanone complex which has a δ_{C-1} of 120.0. While this difference is small, the deshielding is in accord with a structure in which the *p*-nitro group in the cyclopentanone complex bears less negative charge. An increased charge on the *o*-nitro group results in an increased shielding of the ortho carbon (vide infra).

As noted previously, because of the asymmetric carbon exocyclic to the trinitrocyclohexadienate ring in the diethyl ketone, cycloheptanone, cyclohexanone, and cyclopentanone complexes, the two ortho as well as the two meta carbons are not equivalent. These are easily distinguished in the ^{13}C spectra, and the shift values for these, as well as for the para carbon, designated C-1, are summarized in Table II. Values for the acetophenone complexes are difficult to assign because of overlapping aromatic resonances.

It should be noted that the C-1 and C-3 shifts are at substantially *lower* field than the reported shifts for the analogous dimethoxy complex **5**,[9] whereas the C-2 shifts



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are at higher field. This probably means that the negative charge is more evenly distributed on the carbon skeleton in the ketonic complexes. This is in accord with structures in which the bulky ketone moieties in these complexes force the *o*-nitro groups out of the ring plane and diminish their ability to delocalize negative charge.

Both the intrinsic asymmetry of the exocyclic carbon bonded to the anionic ring and the diminished rate of rotation about this bond contribute to the overall nonequivalence of the C-2 and C-3 ring carbons in the ketonic complexes.[8] Since C-3 is closer to the asymmetric site, the effect is greatest on this carbon, and the difference in chemical shift is well over 2 ppm (Table II). The effect at C-2 is less than half that at C-3, and the differences here range from about 0.5 to 1 ppm. What is particularly interesting are changes in the *differences in extent of nonequivalence*, as measured by $\Delta\delta_{2,2'}$ and $\Delta\delta_{3,3'}$ (Table II). The cyclopentanone complex again stands out, having the largest nonequivalence for *both* C-2 and C-3. The values of $\Delta\delta_{2,2'}$ steadily decrease as the ketone becomes more flexible (small ring to large ring to acyclic) whereas the values of $\Delta\delta_{3,3'}$ are relatively unchanged. It appears that, although the effect of asymmetry is greatest at C-3, C-2 is more sensitive to changes in the conformation or bulk of the side chain. At present we have no explanation for this observation.

Experimental Section

All melting points are uncorrected. Visible spectra were recorded on a Perkin-Elmer Model 402 UV-visible spectrophotometer. Kinetic studies were also performed at fixed wavelength on this instrument. ^{13}C NMR spectra were recorded on a Varian XL-100A NMR spectrometer with the samples dissolved in Me_2SO-d_6 (concentration ~0.1 mg/mL). ^1H NMR spectra were run on JEOL C-60 HL and MH-100 spectrometers with Me_4Si as an internal reference. Elemental analyses were obtained from Integral Microanalytical Laboratories, Inc.

sym-Trinitrobenzene was obtained from Eastman and recrystallized from EtOH to a constant melting point (121 °C). All of the ketones were obtained from Aldrich and were used without further purification. Triethylamine was obtained from Eastman and used without further purification. The complexes of the simple acyclic and cyclic ketones were prepared as described previously.[1,2,8]

Complex of Acetophenone and TNB. To a solution of 2.2 g of TNB dissolved in the minimum amount of acetophenone was added 3 mL of triethylamine. The dark red solution was refrigerated for 1 h, and 80 mL of anhydrous Et_2O was then added. After 12 h the dark red crystals which formed were filtered off, ground to a fine powder, washed with copious amounts of anhydrous Et_2O, and dried at 0.5 mm for 24 h at 40 °C. The yield of complex was 3.4 g (78%), mp 86–88 °C (with decomposition). The ^1H NMR spectrum (Me_2SO-d_6) showed the following absorptions: δ 8.5 (2 H, s, cyclohexadienate ring protons), 8.1 (2 H, m, ArH, ortho to carbonyl), 7.7 (3 H, m, J = 4 Hz, ArH), 5.3 (1 H, triplet, J = 3 Hz, cyclohexadienate proton on tetrahedral carbon), 3.2 (8 H, q overlapping d, $HN(CH_2CH_3)_3^+$ and CH_2COAr), 1.3 (9 H, t, $HN(CH_2CH_3)_3^+$). A broad low absorption from δ 6.5 to δ 9.5 accounts for the triethylammonium proton. Anal. Calcd for $C_{20}H_{26}N_4O_7$: C, 55.29; H, 6.03; N, 12.90. Found: C, 55.32; H, 6.09; N, 13.10.

Complex of *p*-Methoxyacetophenone and TNB. This complex was prepared in the same fashion as that described for the acetophenone complex. The pure dry complex had a melting

(8) M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. B*, 147 (1970).
(9) G. Olah and H. Mayr, *J. Org. Chem.*, 41, 3448 (1976).

point of 81–83 °C, and the ^{1}H NMR spectrum (Me_2SO-d_6) showed the following absorptions: δ 8.3 (2 H, s, cyclohexadienate ring protons), 7.9 (2 H, d, J = 4 Hz, ArH ortho to C=O), 7.05 (2 H, d, J = 4 Hz, ArH ortho to OMe), 5.2 (1 H, t, $J \simeq$ 3 Hz, cyclohexadienate proton on tetrahedral carbon), 3.1 (8 H, m, $HN(CH_2CH_3)_3$ overlapping $CH_2COArOMe$), 1.2 (9 H, t, $HN(CH_2CH_3)_3$). This spectrum is poorly resolved because decomposition to starting materials is occurring. This is evidenced by an absorption for TNB at 9.25. The pure complex, mp 81–83 °C, is quite stable however, and analyzes correctly for $C_{21}H_{28}N_4O_8 \cdot 0.5H_2O$: C, 53.27; H, 6.17; N, 11.83. Found: C, 52.96; H, 5.83; N, 11.86.

Complex of *p*-Cyanoacetophenone and TNB. To a solution of 0.96 g of TNB and 1.62 g of *p*-cyanoacetophenone in 25 mL of anhydrous dioxane was added 2 mL of triethylamine. After this mixture was cooled for ~2 h, 100 mL of anhydrous Et_2O was added, and the mixture was kept cold for 12 h. The resulting crystals which formed were filtered, ground to a fine powder, washed with copious amounts of dry Et_2O, and dried at 0.5 mm and 40 °C for 24 h. The ^{1}H NMR spectrum (Me_2SO-d_6) showed the following absorptions: δ 8.55 (2 H, s, cyclohexadienate ring protons), 8.3 (4 H, Ar), 5.3 (1 H, t, J = 4 Hz, cyclohexadienate proton on tetrahedral carbon), 3.1 (8 H, m, $HN^+(CH_2CH_3)_3$ overlapping $CH_2COArCN$), 1.2 (9 H, t, $HN^+(CH_2CH_3)_3$). The complex decomposed over the range of 85–95 °C but analyzed correctly for $C_{21}H_{25}N_5O_7 \cdot 0.75H_2O$: C, 53.33; H, 5.65; N, 14.81. Found: C, 53.13; H, 5.40; N, 14.92.

Complex of *p*-Nitroacetophenone and TNB. This complex was prepared in a fashion similar to that of the *p*-cyanoacetophenone complex. Upon refrigeration, however, the reaction solution formed an oil rather than a crystalline product. The reaction mixture was then diluted to 3 times its original volume with Et_2O and, upon cooling, crystals eventually were formed. These were filtered off, ground to a fine powder, washed with anhydrous ether, and dried at 0.5 mm for 24 h. This product decomposed from 89 to 97 °C. The ^{1}H NMR spectrum (Me_2SO-d_6) showed the following absorptions: δ 8.2 (6 H, symmetrical five-peak multiplet from the single 2 H cyclohexadienate proton absorption centered exactly between the A_2B_2 pattern of the *p*-nitroacetophenone ring), 5.3 (1 H, t, cyclohexadienate proton on tetrahedral carbon), 3.1 (8 H, m, $H^+N(CH_2CH_3)_3^+$ overlapping $CH_2COArNO_2$), 1.2 (t, 9 H, $HN(CH_2CH_3)_3^+$). The melting point was 89–97 °C dec. Anal. Calcd for $C_{20}H_{25}N_5O_9$: C, 50.10; H, 5.26; N, 14.61. Found: C, 49.95; H, 5.37; N, 14.26.

Complex of Cycloheptanone and TNB. This complex was prepared by the previously reported procedure used to prepare the cyclohexanone complex.[8] It had a melting point of 87–90 °C, and the ^{1}H NMR spectrum (Me_2SO-d_6) showed the following absorptions: δ 8.5 (2 H, dd, because of asymmetry at the cycloheptanone ring carbon bonded to the cyclohexadienate moiety, $J \simeq$ 0.5 Hz), 5.1 (1 H, d, cyclohexadienate proton on tetrahedral carbon), 3.18 (6 H, q, $HN(CH_2CH_3)_3^+$), 0.6–2.6 (11 H, m, cycloheptanone protons), 1.2 (9 H, t, $HN(CH_2CH_3)_3^+$, sharp and of greater intensity than that of the cycloheptanone protons which it overlaps). Anal. Calcd for $C_{19}H_{30}N_4O_7$: C, 53.51; H, 7.09; N, 13.14. Found: C, 53.60; H, 7.34; N, 13.21.

Preparation of Buffers. Buffers or HCl solutions were prepared for pH ≃0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, and 6.0. The ionic strength was kept constant at 1.0 by appropriate addition of KCl. The actual pH during a kinetic run was determined by measuring the pH of the buffer in each cuvette before and after injection of the complex (vide infra) and taking the average of these values. Solutions of pH 0–2 were prepared by using the appropriate concentrations of HCl and KCl. The actual measured pH values for runs in this pH region were 0, 0.47, 1.15, 1.48, and 2.08. Buffers in the region of pH 3–5 were made with appropriate concentrations of HOAc, NaOAc, and KCl. Actual measured concentrations for runs in this region were 3.05, 3.95, and 4.97. The pH 6.0 buffer was prepared from appropriate concentrations of Me_2AsO_2H, KOH, and KCl.

Kinetics. The reactions were run at 30 °C and followed spectrophotometrically at 470 nm on a Perkin-Elmer Model 402 spectrophotometer equipped with a thermostated cell holder kept at constant temperature by a Haake constant-temperature circulator. A stock solution of each complex was prepared by dissolving 0.02 g of complex in 1.0 mL of Me_2SO. The pH was measured directly in the cuvette containing buffer. It was then placed in the thermostated cell holder and allowed to equilibrate for at least 15 min. It was quickly removed, and ~5 μL of stock solution was injected (enough to give a large initial absorbance). The cell was quickly stoppered, vigorously shaken for about 5 s, and replaced in the spectrophotometer. The diminishing absorbance at 470 nm was recorded as a function of time with a Fisher Recordall Series 5000 recorder. Even reactions at pH 0 could be followed by using rapid chart speeds. In these instances injections of stock solutions were made into the cuvette in the cell holder. Rapid mixing was achieved with a small plastic spatula and the cell was not stoppered since runs at this pH were completed within 1 min. Two or three runs were made for each complex at each pH.

Rate constants (k_{obsd}) were obtained by using the Guggenheim method. Slopes were calculated by the method of least squares. The absence of acid catalysis for the acetophenone complex decompositions by the acid form of the buffers in the pH range 4–6 should be noted. This is not unexpected because the k_a values are, in general, quite small. Values for k_{HA} are undoubtedly too low to make k_{HA}[HA] significant compared to k_o.

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Registry No. *p*-Methoxyacetophenone–TNB complex, 72318-40-2; acetophenone–TNB complex, 72318-42-4; *p*-cyanoacetophenone–TNB complex, 72318-44-6; *p*-nitroacetophenone–TNB complex, 72318-46-8; cyclopentanone–TNB complex, 53032-21-6; diethyl ketone–TNB complex, 72318-48-0; acetone–TNB complex, 53032-17-0; cycloheptanone–TNB complex, 72318-50-4; cyclohexanone–TNB complex, 72318-52-6.