# Thermodynamic Stabilities of Carbanionic σ Complexes. I. The Reactions of Acetone and Cyclopentanone with 1,3-5-Trinitrobenzene, 1,3-Dinitronaphthalene, and 1,3,6,8-Tetranitronaphthalene

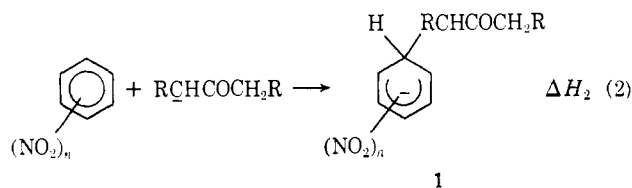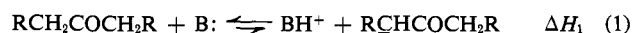## Robert M. Murphy, Claus A. Wulff,* and Michael J. Strauss*

*Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05401. Received November 2, 1973*

**Abstract:** The relative enthalpic stabilities of a series of anionic σ complexes of acetone and cyclopentanone with various polynitroaromatics have been determined. These are the first measured carbanion σ complex stabilities and are of considerable value in comparison with thermodynamic stabilities of complexes prepared with oxygen nucleophiles. Interesting and unexpected stability has been discovered in the case of the cyclopentanone carbanion σ complex of 1,3,5-trinitrobenzene.

The rapidly increasing interest in the chemistry of anionic σ complexes continues unabated. Several reviews appeared in 1968-1970,[1-4] and over 150 reports on the subject have appeared in the literature since that time. Much of this interest has been generated because these complexes are well known as intermediates in nucleophilic aromatic substitution. As with carbonium ion intermediates in solvolytic reactions, much detailed information about the structure and behavior of organic ions in solution can be obtained by investigating the factors which influence their formation and decomposition. In addition, formation of such complexes provides a useful tool for studying nucleophilic reactivity. The factors which influence the stability of such addition complexes in solution have been accumulating steadily in literature reports during the past few years and a clear picture will hopefully emerge shortly. We hope to summarize briefly some of these reports here, and present further clarification with the present studies of carbanionic complex stability.

Most of the reports appearing within the past few years have dealt with kinetic and thermodynamic studies of complexes formed from polynitroaromatics and oxygen nucleophiles.[5-25] Although carbon nucleo-

philes react exothermically to yield quite stable crystalline complexes which have been characterized,[26-40] there have been no quantitative measurements of the stability of such complexes relative to those formed from oxygen nucleophiles. In fact, even the relative stabilities of different carbanionic complexes have not been reported. The reason for this is, in part, that carbanion σ complex formation is usually characterized by a two-step process in which the carbanion is generated in small amounts by a thermodynamically unfavorable equilibrium, followed by an essentially irreversible reaction with aromatic to yield the complex. Such a two-step sequence for simple ketone carbanions is illustrated in eq 1 and 2. We have recently studied the kinetics of

$$RCH_2COCH_2R + B: \ \overset{}{\underset{}{\rightleftharpoons}}\ BH^+ + R\underset{.}{C}HCOCH_2R \qquad \Delta H_1 \quad (1)$$



$$\Delta H_2 \quad (2)$$

this rapid process by stopped-flow spectrophotometric methods.[38] Carbanion complexes of this type form quite readily from ketones,[26-28,38-40] keto esters,[41]

(1) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, 123 (1968).
(2) P. Buck, *Angew. Chem., Int. Ed. Engl.*, 8, 120 (1969).
(3) M. B. Crampton, *Advan. Phys. Org. Chem.*, 7, 211 (1969).
(4) M. J. Strauss, *Chem. Rev.*, 70, 667 (1970).
(5) C. F. Bernasconi, *J. Amer. Chem. Soc.*, 92, 129 (1970).
(6) E. J. Fendler, J. H. Fendler, C. E. Griffin, and J. W. Larson, *J. Org. Chem.*, 35, 287 (1970).
(7) J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, 33, 977 (1968).
(8) C. F. Bernasconi, *J. Amer. Chem. Soc.*, 90, 4982 (1968).
(9) J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, 34, 689 (1969).
(10) F. Terrier, P. Pastour, and R. Schaal, *C. R. Acad. Sci.*, 260, 5783 (1965); *Chem. Abstr.*, 63, 5001f (1965).
(11) J. H. Fendler and E. J. Fendler, *J. Org. Chem.*, 35, 3378 (1970).
(12) J. H. Fendler, E. J. Fendler, and L. M. Casilio, *J. Org. Chem.*, 36, 1749 (1971).
(13) E. J. Fendler and J. H. Fendler, *J. Chem. Soc., Perkin Trans. 1*, 1403 (1972).
(14) E. Buncel and E. A. Symons, *J. Org. Chem.*, 38, 1201 (1973).
(15) M. P. Simonnin, M. J. Lecourt, F. Terrier, and C. A. Dearing, *Can. J. Chem.*, 50, 3558 (1972).
(16) E. Buncel and A. R. Norris, *J. Amer. Chem. Soc.*, 94, 1646 (1972).
(17) C. Bernasconi, *J. Org. Chem.*, 36, 1325 (1971).
(18) F. Terrier, F. Millot, and R. Schaal, *J. Chem. Soc., Perkin Trans. 2*, 1192 (1972).
(19) C. Bernasconi, *J. Amer. Chem. Soc.*, 93, 6975 (1971).

(20) E. A. Symons and E. Buncel, *Can. J. Chem.*, 50, 1729 (1972).
(21) F. Millot, J. Morel, and F. Terrier, *C. A. Acad. Sci., Ser. C*, 274, 23 (1972).
(22) J. Larson and J. H. Fendler, *J. Amer. Chem. Soc.*, 93, 2910 (1971).
(23) J. H. Fendler and J. Larson, *J. Org. Chem.*, 37, 2608 (1972).
(24) F. Millot and F. Terrier, *Bull. Soc. Chim. Fr.*, 11, 3897 (1971).
(25) L. Syper and J. Barycki, *Tetrahedron*, 28, 2233 (1972).
(26) R. Foster and C. A. Fyfe, *J. Chem. Soc. B*, 53 (1966).
(27) R. Foster and C. A. Fyfe, *Tetrahedron*, 22, 1831 (1966).
(28) M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. B*, 147 (1970).
(29) A. R. Norris, *J. Org. Chem.*, 34, 1486 (1969).
(30) M. J. Strauss and R. G. Johanson, *Chem. Ind.*, 8, 242 (1969).
(31) M. J. Strauss, *Tetrahedron Lett.*, 2021 (1969).
(32) C. A. Fyfe, *Can. J. Chem.*, 46, 3047 (1968).
(33) M. Kimura, *Chem. Pharm. Bull. Jap.*, 20, 452 (1972).
(34) O. Wennerstrom, *Acta Chem. Scand.*, 25, 2341 (1971).
(35) R. Wahren, *Acta Chem. Scand.*, 24, 3064 (1970).
(36) K. G. Shipp, L. A. Kaplan, and M. E. Sitzmann, *J. Org. Chem.*, 37, 1966 (1972).
(37) R. P. Taylor, *J. Chem. Soc. D*, 21, 1463 (1970).
(38) M. J. Strauss, H. F. Schran, and R. R. Bard, *J. Org. Chem.*, 38, 3394 (1973).
(39) M. J. Strauss and S. P. B. Taylor, *J. Org. Chem.*, 38, 1330 (1973).
(40) M. J. Strauss and S. P. B. Taylor, *J. Org. Chem.*, 38, 856 (1973).
(41) M. J. Strauss, T. C. Jensen, H. Schran, and K. O'Conner, *J. Org. Chem.*, 35, 383 (1970).

nitroalkanes,[32] and nitriles,[28,30] in the presence of electron deficient aromatics and amines. In fact, such reactions have been the basis for pharmaceutical color tests for many years.[42] For simple ketones, the sum of the enthalpies of reactions 1 and 2 is the experimentally measured enthalpy of formation of the solvated complex 1 from neutral base and aromatic. The value of comparing the enthalpy of formation of complex 1 with that of 1a (R = R′) is limited since both $\Delta H_1$ and $\Delta H_2$ may change (perhaps in opposite directions) as the ketone, i.e., carbanion, is varied. Comparison of such enthalpies of formation of complexes prepared from simple nucleophiles such as ⁻OR or ⁻CN with those for carbanion complex formation is also of little utility since the former are formed in a single-step process. The relative stabilities of carbanionic complexes can be compared if a series of complexes of different aromatics with the same ketone are examined, and we have approached the problem in this way. We have considered relative stabilities of complexes of different ketones with the same aromatic by estimating the "absolute" enthalpies of formation of reactants and products.

In an earlier review of the literature we attempted to estimate the effect of various structural changes on complex stability.[4] These estimates were based on values of $\Delta G$ obtained from equilibrium constant determinations for 1,1-dimethoxy anionic σ complexes reported by Fendler and others.[6−10] The gross approximation necessary to obtain such estimates was that the starting aromatics were of similar free energy. Although such an approximation may not be warranted, the results obtained are surprisingly consistent and are of some predictive value. These are summarized, along with recent new reports,[11,13] in Figure 1. Although some of these values have been rationalized before,[4] it will be instructive to summarize them again for comparison with the present work.

The greater stabilizing effect of the 4-NO₂ relative to the 2-NO₂ probably results from a steric barrier to coplanarity of the ring and 2-NO₂ group in the complex, even though such a barrier should be much less than in both starting aromatics. These ideas are supported by X-ray crystallographic data.[43] The stabilization energy predicted by composite molecule calculations also agrees well with that estimated in Figure 1 for the 2- and 4-NO₂ groups.[44] The calculated difference in resonance energy between a benzene and a cyclohexadienate complex (no NO₂ groups) is 10 kcal, whereas the calculated difference between naphthalene and its C-1 complex (no NO₂ groups) is 2 kcal.[45] The difference in these two values is close to the experimentally measured value of 7.5 kcal[4] which is then the stabilization gained from a benzo fusion.

Recently, the stabilities of 1,1-dimethoxy-2,4,7- and 2,4,5-trinitronaphthalene complexes have been measured.[11,13] These values provide the estimated stabilities for the 5- and 7-NO₂ groups shown in Figure 1. The added stabilizing effect is, as expected, considerably less than for NO₂ groups directly bonded to the ring which undergoes nucleophilic attack. We have ob-
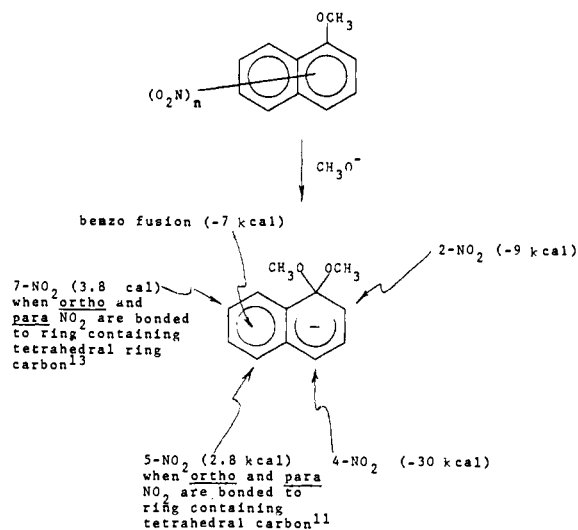
(42) K. A. Kovar, *Pharm. Unserer Z.*, 1, 17 (1972).

(43) R. Destro, C. Gramaccioli, and M. Simonetta, *Acta. Crystallogr.*, 24, 1369 (1968).

(44) H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, 12, 117 (1968).

(45) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p 177.

**Figure 1.** Estimated stabilizing effects ($\Delta G$, kcal) of structural changes in 1,1-dimethoxy polynitroaromatic σ complexes in methanol.[4,6−11,13]

tained these $\Delta G$ values as kilocalories of stabilization relative to the 1,1-dimethoxy-2,4-dinitronaphthalene complex by using the expression
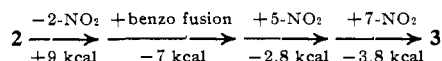
$$\Delta G = RT \ln \{K_{eq}(2,4,7 \text{ or } 2,4,5)/K_{eq}(2,4)\}$$

where the $K_{eq}$ values are those in the literature reports.[11,13] It has been postulated by Fendler that greater effectiveness of C-7 NO₂ relative to C-5 NO₂ in additional stabilization of the parent 2,4-dinitronaphthalene complex probably results from a substantial 4–5 peri interaction forcing the C-4 and C-5 NO₂ out of the ring plane and diminishing the effectiveness of both in delocalizing negative charge.[11,13]

The predictive value of the approximate stabilizations shown in Figure 1 and the remarkable consistency of Fendler's results are apparent when the recently studied 2 and 3 are compared.[12] Although the stabilities of
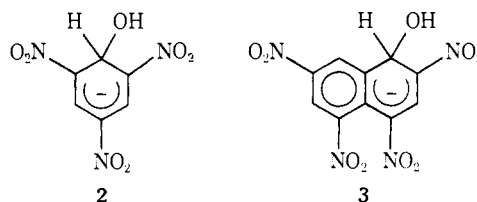


these complexes were measured in water rather than in methanol with the nucleophile hydroxide rather than methoxide and there is no geminal substitution at C-1, the values shown in Figure 1 allow a reasonable prediction of the measured relative equilibrium constants,[12] $K_3/K_2 = 3 \times 10^3$. Starting with 2 the following structural changes can be made to yield 3. The predicted

$$2 \xrightarrow[+9 \text{ kcal}]{-2\text{-NO}_2} \xrightarrow[-7 \text{ kcal}]{+\text{benzo fusion}} \xrightarrow[-2.8 \text{ kcal}]{+5\text{-NO}_2} \xrightarrow[-3.8 \text{ kcal}]{+7\text{-NO}_2} 3$$

value of $K_3/K_2 = 2 \times 10^3$, obtained from expression $RT \ln K_3/K_2 = 4.6$ kcal, is in excellent agreement with that observed experimentally.[12]

We have attempted to verify further the validity of the general stability scheme outlined in Figure 1 by determining relative enthalpic stabilities for a series of polynitroaromatics with carbanions. The results, in large part, substantiate the values in Figure 1 and sup-

port these as being quite useful for predicting poly-nitroaromatic complex stability. The results imply that enthalpic rather than entropic influences are often the primary factors contributing to complex stability.

## Experimental Section

**Materials.** Mallinkrodt reagent grade dimethyl sulfoxide was slurried with $CaH_2$. After standing for at least 24 hr the DMSO was distilled from the slurry through a spinning band column. The distilled samples were stored in flasks sealed with parafilm. Fisher reagent grade triethylamine (TEA) was stirred with phenyl isocyanate for 8 hr and then distilled. The distillate recovered at 89.3° was stored in septum sealed brown bottles covered with layers of parafilm. Fisher reagent grade acetone was used without further purification on the basis of glc and pmr (high spectrum amplitude) analyses which showed no detectable impurities. Baker reagent grade cyclopentanone was distilled and the fraction obtained at 131° was examined by glc and shown to be pure. A crude sample of Eastman *sym*-trinitrobenzene (TNB) was recrystallized five times from anhydrous ethanol. The crystals obtained were dried in a vacuum oven and melted at 121–122° (lit.[46] 121°). Aldrich 2,4-dinitronaphthalene (DNN) was recrystallized three times from benzene and, after drying in a vacuum oven, melted at 146–148° (lit.[46] 144–145°). Aldrich 1,8-dinitronaphthalene was nitrated according to the reported procedure[12] to give good yields of 1,3,6,8-tetranitronaphthalene (TNN), mp 205° (lit.[12] 203–205°).

**Calorimetry.** Measurements reported were obtained using the commercial LKB 8700-1 calorimetry system.[47] Because of the small energy evolutions involved, particular attention was given to the temperature stability of the calorimeter environment. The system was maintained in a thermostated room, regulated to within ±1° at 23°. The LKB 7600A/18 precision thermostat is cooled by water circulated from a Haake Model FJ circulation unit which in turn is fed by a cooled supply from a Sargent water bath cooling unit. The cascading effect of the three regulated baths maintained the calorimeter environment of 25.01° (nominal) with a short term (3 hr) stability of ±0.0002°. The temperature within the 8700A/18 thermostat was monitored continuously with a Hewlett-Packard 2801A quartz thermometer.

All experiments were carried out in a single 100-ml calorimeter of the standard design. To reduce experimental variations, the calorimeter was left in place for all reported runs, and the mechanical ampoule-breaking device was employed. All ampoules used were the commercial LKB 8727-2 with a nominal capacity of 1 ml.

Two types of calorimetric experiments were carried out, referred to hereafter as dilutions and reactions. Dilution experiments were run to determine the "ampoule-breaking correction." Included in this term are the heat evolutions engendered by (a) the mechanical fragmentation of the ampoule, (b) the vaporization of solvent to fill the vapor space of the partially filled ampoule, and (c) the dilution of solvent mixtures by additional DMSO. Of these, c is the most significant. For each dilution run the solvent was 90 ml of DMSO, 5 ml of TEA, and 5 ml of the appropriate ketone. Such "solvents" were stable for about 8 hr. Aldol type condensations of acetone did not occur during the time necessary for a dilution or reaction run. All volumes were measured by pipet or syringe with a minimal precision of ±1%. Ampoules were filled with 1-g (±0.05) samples of DMSO. The results are summarized in Table I.

Reactions were carried out in the same manner as dilutions except that the ampoules contained solutions of nitroaromatic substrate dissolved in DMSO. The solutions were prepared by mass to given concentrations of about 0.04 mol kg$^{-1}$ of aromatic in DMSO. All ampoules needed for a given series were prepared and sealed before the reaction runs were begun. The results are summarized in Tables II and III. In these tables the quantity $q$ represents the observed heat evolutions and $q'$ the dilution correction determined from the dilution runs for the appropriate ketone-solvent mixture. The molal enthalpy of reaction, $\Delta H$, is determined as $\Delta H = (q - q')/n$. Values of $\Delta T$ were determined from computer-generated least-squares fits through the resistance-time data for the fore- and after-rating periods. The apparent reaction half times were determined from large scale plots of the data in the form of $[1/R][\Delta R/\Delta t]$ against $R$ and of $R$ against $t$. Details of the data analysis may be found elsewhere.[48] Times required for

(46) "Heilbronners Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965.
(47) S. Sunner and I. Wadso, *Sci. Tools*, **13**, 1 (1966).
(48) R. M. Murphy, Thesis, University of Vermont, 1973.

**Table I.** Dilution Series for Acetone and Cyclopentanone in DMSO, TEA, and Ketone

| Mass DMSO, g | $\Delta T$,[a] $10^3 \alpha$ | $C_{sys}$,[b] cal $\alpha^{-1}$ | $\bar{q}$,[c] cal g$^{-1}$ |
|---|---|---|---|
| | Acetone | | |
| 0.94557 | −1.28 | 54.0 | 0.073 |
| 0.94270 | −1.09 | 50.8 | 0.059 |
| 1.01796 | −1.43 | 51.2 | 0.072 |
| 0.94627 | −1.25 | 51.0 | 0.067 |
| 1.06984 | −1.24 | 51.2 | 0.059 |
| 1.05620 | −1.28 | 53.0 | 0.064 |
| 1.01667 | −1.09 | 50.3 | 0.054 |
| 1.03646 | −1.12 | 54.2 | 0.059 |
| | Mean ± rms deviation | | 0.063 ± 0.007 |
| | Cyclopentanone | | |
| 0.96890 | −0.98 | 49.6 | 0.050 |
| 1.02171 | −1.35 | 50.2 | 0.066 |
| 1.05546 | −1.26 | 50.5 | 0.060 |
| 1.02407 | −1.52 | 50.9 | 0.076 |
| 0.95310 | −1.20 | 51.0 | 0.064 |
| | Mean ± rms deviation | | 0.063 ± 0.008 |

[a] Data gathered with the LKB-8700 series is not appropriate for direct temperature conversion. $1 \alpha \simeq 1°$ based on the characteristics of the thermistor that $70 \Omega \simeq 1°$ at 25°. [b] Heat capacity of the system. [c] Heat evolved.

**Table II.** Reaction Series for Acetone

| Mass DMSO, g | Mol Ar, $10^5$ | $\Delta T$, $10^3 \alpha$ | $C_{sys}$, cal $\alpha^{-1}$ | $q$, cal | $q'$, cal | $\Delta H$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | DNN | | | |
| 0.88915 | 3.836 | 0.52 | 50.3 | −0.026 | 0.056 | −2.1$_4$ |
| 0.96936 | 4.182 | 0.64 | 50.3 | −0.032 | 0.061 | −2.2$_2$ |
| 0.94533 | 4.078 | 0.79 | 51.1 | −0.040 | 0.060 | −2.4$_6$ |
| 0.83383 | 3.597 | 0.60 | 49.7 | −0.030 | 0.053 | −2.3$_0$ |
| | | | Mean ± rms deviation | | | −2.3 ± 0.1 |
| | | | TNB | | | |
| 0.91507 | 4.299 | 3.10 | 49.6 | −0.154 | 0.058 | −4.9$_2$ |
| 0.98190 | 4.613 | 3.81 | 51.5 | −0.196 | 0.062 | −5.6$_0$ |
| 1.00209 | 4.707 | 3.53 | 50.2 | −0.177 | 0.063 | −5.1$_0$ |
| 1.03098 | 4.843 | 3.37 | 51.4 | −0.173 | 0.065 | −4.9$_2$ |
| 0.91010 | 4.275 | 2.96 | 51.7 | −0.153 | 0.058 | −4.9$_3$ |
| | | | Mean ± rms deviation | | | −5.1 ± 0.3 |
| | | | TNN | | | |
| 0.90919 | 3.617 | 15.9 | 50.5 | −0.802 | 0.058 | −23.7$_8$ |
| 0.99200 | 3.946 | 18.1 | 50.1 | −0.907 | 0.063 | −24.5$_5$ |
| 0.99007 | 3.938 | 17.6 | 50.2 | −0.884 | 0.063 | −24.0$_2$ |
| 0.95002 | 3.779 | 17.1 | 50.4 | −0.862 | 0.060 | −24.3$_9$ |
| | | | Mean ± rms deviation | | | −24.2 ± 0.3 |

completion of the reaction ranged from 7 to 24 min for the several series, the longest being those for the reactions of acetone with tetranitronaphthalene. It is recognized that the total heat evolutions are small and hence serve to magnify inherent uncertainties in the method. Attempts to increase the magnitudes by use of larger samples failed because of the extremely long reaction times required. There is no question that at the high concentrations of amine and ketone we have used (relative to aromatic) that all reactions are complete.

**Structural Characterization of the Complexes.** The $\sigma$ complex of triethylamine, acetone, and TNB has been prepared previously and characterized.[26] We have isolated and characterized the crystalline complex of triethylamine, acetone, and TNN.[49] The analogous complex of DNN has also been characterized.[32] The cyclopentanone complex of TNB has been studied by pmr,[28] and the TNN and DNN complexes with this ketone have been prepared and characterized.[49] In the complexes of DNN and TNN attack of carbanion always occurs at the unsubstituted peri position para to an $NO_2$ group. This is entirely analogous to the behavior of a

(49) Details of this work will be published elsewhere.

**Table III.** Reaction Series for Cyclopentanone

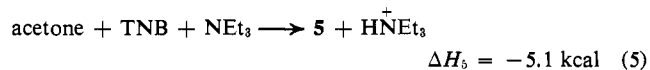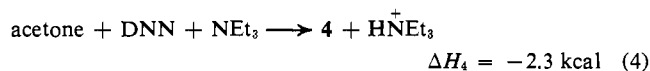| Mass DMSO, g | Mol Ar, $10^5$ | $\Delta T$, $10^3$ $\alpha$ | $C_{sys}$, cal $\alpha^{-1}$ | $q$, cal | $q'$, cal | $\Delta H$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | DNN | | | |
| 0.97984 | 4.227 | 4.22 | 50.2 | −0.212 | 0.062 | −6.4$_7$ |
| 1.01522 | 4.379 | 4.13 | 50.3 | −0.208 | 0.064 | −6.2$_0$ |
| 0.73342 | 3.164 | 2.86 | 50.2 | −0.144 | 0.046 | −5.9$_8$ |
| | | | Mean ± rms deviation | | | −6.2 ± 0.2 |
| | | | TNB | | | |
| 0.99751 | 4.686 | 24.4 | 49.4 | −1.204 | 0.063 | −27.0$_4$ |
| 1.00878 | 4.739 | 23.7 | 51.2 | −1.214 | 0.064 | −26.9$_5$ |
| 1.00345 | 4.714 | 24.3 | 50.4 | −1.224 | 0.064 | −27.3$_6$ |
| 1.02172 | 4.800 | 25.1 | 49.6 | −1.244 | 0.065 | −27.2$_9$ |
| | | | Mean ± rms deviation | | | −27.2 ± 0.2 |
| | | | TNN | | | |
| 0.90530 | 3.601 | 18.7 | 51.9 | −0.970 | 0.057 | −28.5$_4$ |
| 0.94880 | 3.774 | 19.6 | 51.2 | −1.004 | 0.060 | −28.2$_1$ |
| 1.01876 | 4.053 | 21.4 | 50.0 | −1.070 | 0.065 | −28.0$_2$ |
| 1.03300 | 4.109 | 21.7 | 49.7 | −1.080 | 0.065 | −27.8$_2$ |
| 1.00849 | 4.012 | 21.8 | 49.7 | −1.084 | 0.064 | −28.6$_1$ |
| | | | Mean ± rms deviation | | | −28.2 ± 0.3 |

variety of other nucleophiles which form complexes with these aromatics and is not unexpected.[1-4] Even if C-3 attack occurred initially, followed by rearrangement to the C-1 (peri) complex, the value of $\Delta H$ would remain unchanged. The appearance of the resistance-time curves leads us to believe that such processes are not occurring.

## Discussion

**(1) Variation of the Aromatic.** From Figure 1, $\Delta G$ for the exchange reaction 3 can be estimated as
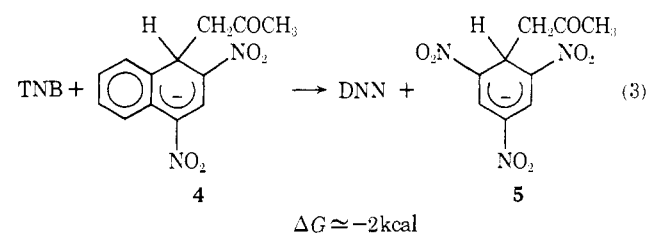


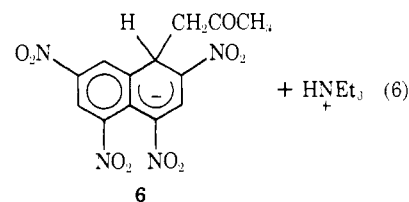$$\Delta G \simeq -2\text{kcal}$$

$\sim -2$ kcal. This estimate is essentially derived from the experimentally obtained values of $\Delta G$ obtained by Fendler for the formation of the geminal 1,1-dimethoxy complexes of the related anisoles.[7] We have obtained the following enthalpies of reaction for *formation* of **4** and **5** from acetone, aromatic, and amine in DMSO solu-

$$\text{acetone} + \text{DNN} + \text{NEt}_3 \longrightarrow 4 + \text{HNEt}_3^+$$
$$\Delta H_4 = -2.3 \text{ kcal} \quad (4)$$

$$\text{acetone} + \text{TNB} + \text{NEt}_3 \longrightarrow 5 + \text{HNEt}_3^+$$
$$\Delta H_5 = -5.1 \text{ kcal} \quad (5)$$

tion (see Experimental Section). Combining eq 4 and 5, the enthalpy for the **4–5** exchange indicated in eq 3 is $\Delta H_3 = \Delta H_5 - \Delta H_4 = -2.8 \pm 0.3$ kcal. Comparison of $\Delta G_3$ and $\Delta H_3$ indicates that the enhanced stability of **5** is largely an enthalpy effect and *differences in complex conformation which might be expected to influence* $\Delta S$ *are minor.* This is not unexpected, since the environments about the tetrahedral carbons in **4** and **5** which now bear the added nucleophile are similar. The situation is quite different for the tetranitronaphthalene complex.

The heat of reaction of acetone with TNN has been measured (see Experimental Section). Combining eq

5 and 6, the enthalpy for the exchange (7) can be cal-

$$\text{acetone} + \text{TNN} + \text{NEt}_3 \longrightarrow$$
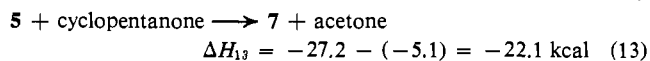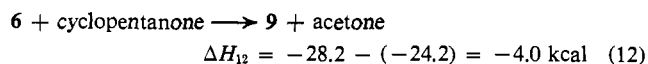


$$6$$
$$\Delta H_6 = -24.2 \text{ kcal}$$

$$5 + \text{TNN} \longrightarrow 6 + \text{TNB} \qquad \Delta H_7 = -19.1 \text{ kcal} \quad (7)$$
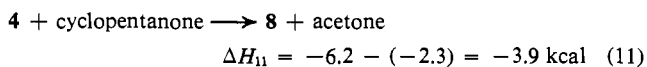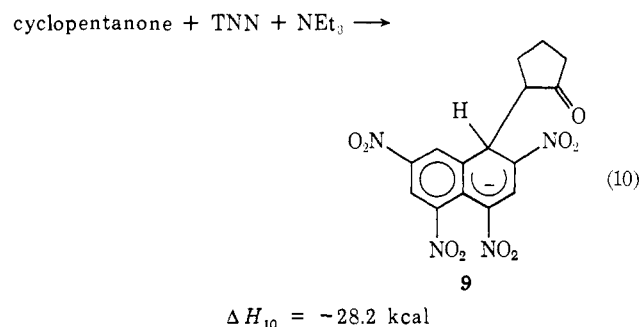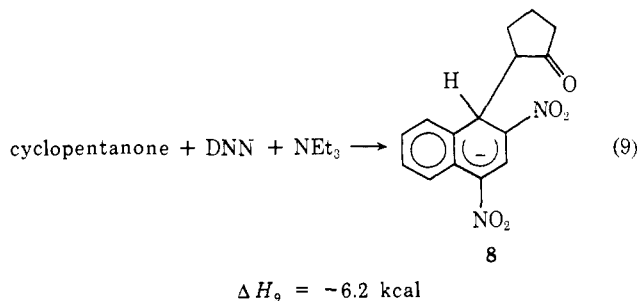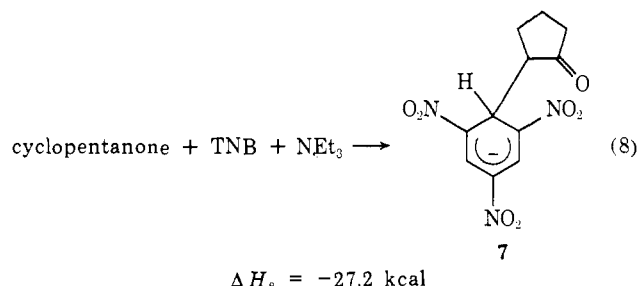
culated as −19.1 kcal. From Figure 1 the predicted value of $\Delta G_7$ is −4.4 kcal, which is also very close to the experimentally obtained value for the increased stability of the analogous hydroxy complex **3** over **2**, reported by Fendler.[12] A comparison of $\Delta G_7$ and $\Delta H_7$ shows that the latter is some 15 kcal more exothermic than would have been expected if oxygen and carbon base complexes behave similarly. If this is the case, the smaller value of $\Delta G$ results from a considerable entropy increment. Although there are many uncertainties involved in the estimate of $\Delta G_7$, the peri interactions of the C-5 and C-7 NO$_2$ groups could well be quite important. Any orthogonality of these groups with the ring will place more charge on the two remaining NO$_2$ groups, one of which is adjacent to the acetonate moiety. The effects of a more rigid solvent structure about the C-2 NO$_2$ and increased rotational restrictions about the C-1 acetonate bond could account, in part, for such an entropy increment. Fendler has pointed out that entropic factors are of considerable importance in the formation and decomposition of related 1,1-dimethoxy complexes.[11,13] Alternately, it could be that as the numbers of systems investigated increases the parallel behavior of oxygen and carbon base complexes will not be as consistent as initially predicted. If such is the case, there may not be a tremendous discrepancy between $\Delta H_7$ and $\Delta G_7$. Data on many more systems are needed before truely definitive conclusions can be reached.

Specific orientations of the ketonic moiety may be of considerable importance in determining carbanion complex stability. Such effects may be reflected in the differing heats of exchange when acetone and cyclopentanone complexes are compared. These comparisons will now be considered.

**(2) Variation of the Ketone.** The enthalpies determined for the formation of the cyclopentanone complexes of the various aromatics are summarized in eq 8, 9, and 10. The appropriate enthalpies of acetone-cyclopentanone exchange can be obtained by combining eq 8–10 with 4–6, and the results of such combinations are summarized in eq 11, 12, and 13, *i.e.*, eq 11 = eq 8 − eq 4. One interpretation of these competitive reaction enthalpies can be given in terms of "absolute" enthalpies of formation. The experimental $\Delta H$ for the exchange reactions 11–13, involving a common aromatic, is represented by the quantity

$$\Delta H_{exch} = [\Delta H_f(\text{cyclopentanone complex}) -$$

$$\Delta H_f(\text{acetone complex})] - [\Delta H_f(\text{acetone}) -$$

$$\Delta H_f(\text{cyclopentanone})]$$

cyclopentanone + TNB + NEt$_3$ $\longrightarrow$



**7**

$$\Delta H_8 = -27.2 \text{ kcal}$$

cyclopentanone + DNN + NEt$_3$ $\longrightarrow$



**8**

$$\Delta H_9 = -6.2 \text{ kcal}$$

cyclopentanone + TNN + NEt$_3$ $\longrightarrow$



**9**

$$\Delta H_{10} = -28.2 \text{ kcal}$$

**4** + cyclopentanone $\longrightarrow$ **8** + acetone

$$\Delta H_{11} = -6.2 - (-2.3) = -3.9 \text{ kcal} \quad (11)$$

**6** + cyclopentanone $\longrightarrow$ **9** + acetone

$$\Delta H_{12} = -28.2 - (-24.2) = -4.0 \text{ kcal} \quad (12)$$

**5** + cyclopentanone $\longrightarrow$ **7** + acetone

$$\Delta H_{13} = -27.2 - (-5.1) = -22.1 \text{ kcal} \quad (13)$$

The second bracketed quantity can be evaluated from literature data[50] as $-3$ kcal/mol if it is assumed that the heats of solution of the two ketones in DMSO are comparable. With this assumption, the difference in enthalpies of formation between the acetone complexes of DNN and TNN, as well as the difference in enthalpies of formation of the cyclopentanone complexes of these two aromatics, is only about 1 kcal/mol in each case.

The situation is quite different for the competitive reaction involving TNB. Comparison of $\Delta H_{13}$ with $\Delta H_{11}$ and $\Delta H_{12}$ shows an enhanced enthalpic stability of some 18 kcal/mol for **7**. In an earlier report[28] we have commented about the unusual pmr characteristics of **7** which provided considerable evidence for some sort of interaction between the ketonic moiety and adjacent NO$_2$ groups. In that report we considered the possibility of steric repulsion of the carbon framework of the cyclopentanone ring and the adjacent NO$_2$ groups. Such a barrier may in fact result from a strong and *stabilizing* dipole attraction between the carbonyl and one of the two NO$_2$ functions. Such an explanation is supported by the unusual enthalpic stability of **7**.

(50) J. D. Cox and G. Pilchen, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London, 1970.

# Solvation of Ions. XXI.[1] Solvation of Potassium Cation in Nonaqueous Solvents

Dwain Alan Owensby, A. J. Parker,* and John W. Diggle

*Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. Australia. Received September 29, 1973*

**Abstract:** The free energies of transfer of potassium cation from water to 14 nonaqueous solvents are reported. The values are derived from measurements in an electrochemical cell assumed to have a negligible liquid junction potential and are compared with existing literature values based on the assumption that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(BPh_4^-)$. The essentially electrostatic nature of its solvation allows potassium cation to be used as a model for nonspecific solvent–ion interactions. A comparison of $\Delta G_{tr}(Ag^+)$ with $\Delta G_{tr}(K^+)$ detects some specific interactions of the silver cation with solvents. Especially noteworthy in this regard is the striking difference between $\Delta G_{tr}(Ag^+)$ of $-23.8$ kcal mol$^{-1}$ and $\Delta G_{tr}(K^+)$ of $+6.4$ kcal mol$^{-1}$ for transfer from water to dimethylformthioamide at 25°.

As with other simple spherical univalent cations of closed electron shells, the solvation of potassium cation is best described in terms of the electrostatic interaction between the ion and polar solvent molecules, modified by the effect of the ion on solvent–solvent interactions (solvent structure). The potassium cation is

"hard" in the Pearson sense,[2] having a size ($r_c = 1.33$ Å) intermediate between that of the very small lithium ion ($r_c = 0.68$ Å) and the large cesium ion ($r_c = 1.67$ Å). The ion–solvent interactions, of course, are modified somewhat by the effect of the ion on the solvent–solvent interactions, i.e., by the solvent structure. Because covalent interactions between potassium cation and sol-

(1) Part XX: J. W. Diggle and A. J. Parker, *Electrochim. Acta*, 18, 975 (1973).

(2) R. G. Pearson, *J. Amer. Chem. Soc.*, 85, 3533 (1963).