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# The Resonance Energy of Cycloheptatrienyl Radical

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**Abstract:** The homolytic thermal cleavage of neat liquid bitropenyl (bi-2,4,6-cycloheptatrien-1-yl) to form the cycloheptatrienyl (tropenyl) radical, $C_7H_7\cdot$, has been investigated by means of electron spin resonance spectroscopy. The enthalpy of this dissociation reaction, $\Delta H° = 35 \pm 1$ kcal/mole, has been evaluated from the variation of the intensity of the hyperfine components of $C_7H_7\cdot$ as a function of temperature. Using this value of $\Delta H°$ the "extra" resonance energy (RE) of $C_7H_7\cdot$ is estimated to be 21 kcal/mole and the total empirical RE to be 31 kcal/mole. Comparison of this result with previous work reveals that tropenyl radical is among the most extensively resonance-stabilized free radicals. From the measured value of $\Delta H°$ other thermochemical quantities are estimated, namely $\Delta H_f°(C_7H_7\cdot(g)) = 65$ kcal/mole, $\Delta H_f°(C_7H_7^+(g)) = 209$ kcal/mole, $RE(C_7H_7^+(g)) = 58$ kcal/mole, and $D(C_7H_7{-}H) = 73$ kcal/mole. Empirical resonance energies are correlated with calculated delocalization energies.

The resonance stabilization of $\pi$-electron hydrocarbon molecules is a subject of general interest and considerable activity.[4,5] Relatively few free radicals have been investigated experimentally to date.

In this work we have evaluated the empirical resonance energy (RE) of the cycloheptatrienyl (tropenyl) radical, $C_7H_7\cdot$.[6] The method employed involves a measurement of the enthalpy of cleavage of bitropenyl using esr spectroscopy. The application of this technique to the determination of a resonance energy is novel.

Our principal result is that the total empirical RE is 31 kcal/mole. Comparison with previous studies of free radicals reveals that the tropenyl radical is stabilized by resonance to an unusually high degree.

## Results

The homolytic thermal cleavage of neat liquid bitropenyl (bi-2,4,6-cycloheptatrien-1-yl)

$$C_7H_7{-}C_7H_7 \overset{\Delta}{\rightleftharpoons} 2C_7H_7\cdot \qquad (1)$$

has been investigated by means of esr spectroscopy and the enthalpy change, $\Delta H°$, for this reaction has been evaluated. The resonance energy of $C_7H_7\cdot$ is computed using this value of $\Delta H°$. Below we develop the equation relating $\Delta H°$ to the esr data.

**Relationship between $\Delta H°$ and the Esr Signal Intensity.** The equilibrium constant for reaction 1 is given by

$$K = (a_{A\cdot})^2/a_{A_2} \qquad (2)$$

where the dimer (bitropenyl) and radical are designated $A_2$ and $A\cdot$, respectively, and where $a_{A_2}$ and $a_{A\cdot}$ are the corresponding activities. In another study we have found that the concentration of tropenyl radical in equilibrium with neat bitropenyl at 406°K is only $\approx 10^{-6}$ *M*.[7] We are therefore led to conclude that (1) the activity of the dimer, which is essentially a pure liquid, is unity, (2) Henry's law holds for the radical

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(3) Deceased April 3, 1968.

(4) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(5) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966.

(6) Other esr studies of the tropenyl radical and substituted tropenyl radicals include: (a) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, Jr., and F. R. Hunter, *J. Am. Chem. Soc.*, **87**, 3527 (1965); (b) G. Vincow, *J. Chem. Phys.*, 47, 2774 (1967); (c) G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *ibid.*, **48**, 2876 (1968); (d) W. V. Volland and G. Vincow, *ibid.*, **48**, 5589 (1968).

(7) W. V. Volland, Ph.D. Thesis, University of Washington, 1967.

(solute), and (3) the density of the solution is equal to that of the dimer (solvent).

Substitution of the Henry's law expression into the definition of the activity of the solute leads to

$$a_{\mathrm{A}\cdot} = X_{\mathrm{A}\cdot} \cong c_{\mathrm{A}\cdot}M_{\mathrm{A}_2}/1000\rho_{\mathrm{A}_2}(T) \tag{3}$$

where $X_{\mathrm{A}\cdot}$ and $c_{\mathrm{A}\cdot}$ are the mole fraction and concentration (moles liter$^{-1}$) of the radical, respectively, $M_{\mathrm{A}_2}$ is the molecular weight of the dimer, and $\rho_{\mathrm{A}_2}(T)$ is its density. The standard state of the solute is the hypothetical state of unit mole fraction and fugacity equal to the Henry's law constant.[8]

Combining (3) and $a_{\mathrm{A}_2} = 1$ with (2) gives

$$K = c_{\mathrm{A}\cdot}^{2}M_{\mathrm{A}_2}^{2}/10^{6}\rho_{\mathrm{A}_2}^{2}(T) \tag{4}$$

Substitution of (4) into the van't Hoff equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2} \tag{5}$$

followed by integration, results in

$$2\ln c_{\mathrm{A}\cdot}(T) - 2\ln \rho_{\mathrm{A}_2}(T) = -\Delta H^\circ/RT + \text{constant} \tag{6}$$

where $\Delta H^\circ$ is assumed to be constant over the 20°K temperature interval employed in this work.

The concentration of free radicals, $c_{\mathrm{A}\cdot}(T)$, which appears in eq 6, is readily related to the measured intensity of the esr spectrum. We assume that Curie's law holds for $\mathrm{C_7H_7}\cdot$ (since its concentration is $\approx 10^{-6}M$). Then, $c_{\mathrm{A}\cdot}(T)$ is proportional to the area under the esr absorption curve and to the absolute temperature. In this work *first derivative* spectra are obtained. In terms of the parameters of the first derivative spectrum, the area under the absorption curve is proportional to $kw^2h$ where $k$ is a constant characteristic of the lineshape and $w$ and $h$ are the full peak-to-peak width and peak-to-peak amplitude, respectively, of a particular component. Within our experimental error ($\pm 5\%$), the width $w$ of one of the central components of the $\mathrm{C_7H_7}\cdot$ spectrum is independent of temperature ($120 \leq t \leq 140°$). Further, we make the reasonable assumption that $k$ is independent of temperature. Then $c_{\mathrm{A}\cdot}(T)$ is proportional to $hT$ and eq 6 can be rewritten to give

$$2\ln hT - 2\ln \rho_{\mathrm{A}_2}(T) = -\Delta H^\circ/RT + \text{constant}' \tag{7}$$

This is the equation which has been used in order to evaluate $\Delta H^\circ$.

**Experimental Value of $\Delta H^\circ$.** The data required for the evaluation of $\Delta H^\circ$ are the amplitudes of the esr spectra at various temperatures and the density of liquid bitropenyl as a function of temperature.

Signal amplitudes ($h$) have been measured as a function of temperature for the two central components of the $\mathrm{C_7H_7}\cdot$ spectrum. For each run numerous amplitude measurements have been made at each of two temperatures in the range $120 \leq t \leq 140°$.[9]

The upper limit to the temperature which can be employed in this study, 140°, is determined by the kinetics of a competitive irreversible process, the intramolecular thermal isomerization of bitropenyl. At 140° the $\mathrm{C_7H_7}\cdot$ peak height decays with a first-order half-life of 30 hr.[10] We have therefore restricted the duration of our runs to 1 hr or less.

The density of bitropenyl, required in eq 7, has been measured. Our result is

$$\rho_{\mathrm{A}_2}(T) = 1.015 - 0.75 \times 10^{-3}(T - 333) \tag{8}$$

and the estimated maximum limits of error in the slope and intercept are $\pm 0.25 \times 10^{-3}$ and $\pm 0.02$, respectively.

Ten determinations of $\Delta H^\circ$ have been made. For each a linear least-squares analysis of $\{2\ln hT - 2\ln[1.015 - 0.75 \times 10^{-3}(T - 333)]\}$ *vs.* $T^{-1}$ has been performed. The values of $\Delta H^\circ$ obtained from each run are listed in Table I along with error estimates, upper and lower limits of temperature, and the number of amplitude measurements. The average value obtained from the ten determinations is 35.0 kcal/mole.[11] An estimated precision measure (95% confidence interval) is ±0.5 kcal/mole and conservative maximum limits of error are ±1.0 kcal/mole.

**Table I.** Results of Ten Determinations of $\Delta H^\circ$ for the Thermal Cleavage of Neat Liquid Bitropenyl

| $\Delta H^\circ$, kcal/mole | Temp,[a] °K High | Temp,[a] °K Low | No. of amplitude measurements |
|---|---|---|---|
| 34.0 ± 1.3[b] | 405 | 386 | 36 |
| 33.7 ± 0.8 | 405 | 385 | 24 |
| 34.4 ± 0.8 | 403 | 394 | 21 |
| 34.8 ± 0.5 | 411 | 391 | 18 |
| 36.0 ± 1.2 | 406 | 395 | 26 |
| 35.8 ± 1.8 | 412 | 394 | 23 |
| 34.5 ± 0.9 | 412 | 398 | 27 |
| 35.6 ± 0.6 | 409 | 396 | 26 |
| 34.8 ± 0.6 | 412 | 398 | 28 |
| 36.2 ± 0.5 | 417 | 401 | 24 |

[a] These values are the upper and lower limits of the temperatures employed in each run. [b] An error estimate, based on twice the standard deviation of the slope of the least-squares fit of eq 7.

It is interesting to note that, on the basis of mass spectrometric evidence, Harrison, Honnen, Dauben, and Lossing[12] estimated the value 35 ± 7 kcal/mole for the dissociation energy of bitropenyl. The agreement with this work is excellent.

## Discussion

**Empirical Resonance Energy of Tropenyl Radical.** From the results presented in the previous section we note that the central CC bond in bitropenyl has an extremely small bond dissociation energy (≈35 kcal/mole). By way of comparison, corresponding values in ethane, biisopropyl, and bibenzyl are about 50, 43, and 25 kcal/mole larger, respectively. We ascribe this weak bond in bitropenyl to resonance stabilization of the tropenyl radicals formed in the homolysis.[13]

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(8) I. M. Klotz, "Chemical Thermodynamics," W. A. Benjamin, Inc., New York, N. Y., 1964, p 351.

(9) In preliminary work data was taken at a number of temperatures, and the linearity of $[2\ln hT - 2\ln \rho_{\mathrm{A}_2}(T)]$ *vs.* $T^{-1}$ was verified.

(10) W. V. Volland and G. Vincow, *J. Am. Chem. Soc.*, **90**, 4537 (1968).

(11) If the temperature dependence of the density of bitropenyl is neglected, an average value of $\Delta H^\circ = 34.5$ kcal/mole is obtained. Since the density effect changes $\Delta H^\circ$ by only 0.5 kcal/mole (1.4%), our rather approximate measurement of the density is satisfactory.

(12) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

(13) The contribution of steric repulsion in the dimer to the lowering of the enthalpy of cleavage is assumed to be small and is neglected.

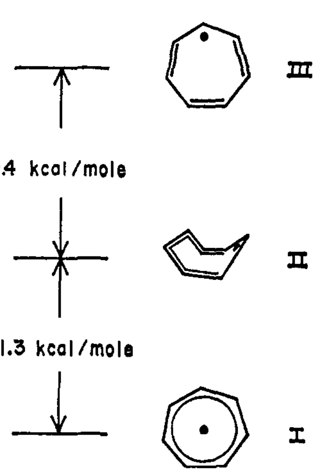


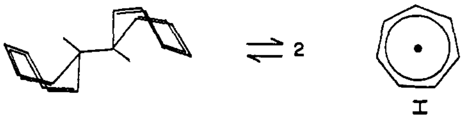
Figure 1. Differences between the enthalpies of formation ($\Delta H_f°$) of the tropenyl radical (I) and of various structures (see text for detailed descriptions).

On the basis of this assumption, the empirical resonance energy of $C_7H_7\cdot$ can be estimated (see Figure 1). The resonance energy is given by

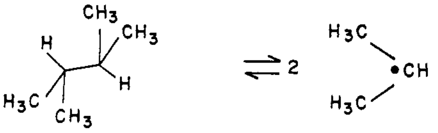
$$\mathrm{RE} \equiv |\Delta H_f°(\mathrm{I}) - \Delta H_f°(\mathrm{III})| \qquad (9)$$

where I is the tropenyl radical, assumed planar, and symmetrical in accordance with previous esr investigations,[6] and III is the hypothetical planar radical with the unpaired electron localized and three noninteracting double bonds.

We proceed in two stages. First we determine the difference between the enthalpies of formation of I and II; II denotes a hypothetical structure with the $\sigma$-bond framework of cycloheptatriene, a delocalized triene $\pi$ system, and an unpaired electron localized on the carbon atom corresponding to the methylene carbon of cycloheptatriene. This enthalpy difference is estimated by consideration of the following gas-phase equations.

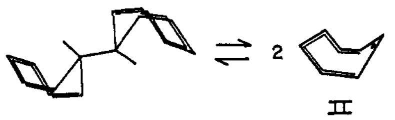


$\Delta H_1$ = 35 kcal/mole



$\Delta H_2$ = 77.7 kcal/mole[14]

In addition we assume that the enthalpy of the following hypothetical cleavage is equal to that of biisopropyl.



$\Delta H_3 = \Delta H_2$[15,16]

$$\Delta H_f°(\mathrm{I}) - \Delta H_f°(\mathrm{II}) = \frac{1}{2}[\Delta H_1 - \Delta H_2] = \frac{1}{2}[35 - 77.7] = -21.3 \text{ kcal/mole} \qquad (10)$$

In using the value 35 kcal/mole above we have neglected (1) the difference between the enthalpy of dissociation in the gas phase and in the neat liquid, and (2) the temperature dependence of $\Delta H_1$. It is estimated that this leads to an uncertainty in the resonance energy of approximately 2 kcal/mole.

The next quantity determined is $\Delta H_f°(\mathrm{II}) - \Delta H_f°(\mathrm{III})$. This enthalpy change is approximated by the empirical resonance energy of cycloheptatriene, a quantity computed from heat of hydrogenation results to be 9.8[17-19] and 9.0 kcal/mole[18,19] in the gas phase and in acetic acid solution, respectively.

Adding the average of these values to eq 10, we obtain 31 kcal/mole (±4 kcal/mole estimated error) for the total empirical resonance energy of the tropenyl radical. The main conclusion to be drawn from this result is that $C_7H_7\cdot$ is an extensively resonance-stabilized molecule and should therefore be considered aromatic. Its RE is, in fact, almost equal to that of benzene, which is 36 kcal/mole.[4,5]

We can also compare our result with those obtained for other hydrocarbon free radicals. The most valid comparison is made by considering not the total empirical RE but the "extra" resonance energy obtained by the delocalization of the unpaired electron.[20] In the case of $C_7H_7\cdot$ this is given by $|\Delta H_f°(\mathrm{I}) - \Delta H_f°(\mathrm{II})| = 21$ kcal/mole.

"Extra" resonance energies of a number of hydrocarbon free radicals are listed in Table II. The "extra" RE of $C_7H_7\cdot$ is almost as large as that of cyclohexadienyl and is greater than the values for triphenylmethyl, pentadienyl, benzyl, and allyl radicals. It would thus appear that the tropenyl radical is one of the most resonance-stabilized free radicals investigated to date.

The considerable magnitude of the "extra" RE of $C_7H_7\cdot$ also indicates that this radical should be very unreactive, since the "extra" RE represents an energy price which the tropenyl radical would have to pay in order to participate in many types of reactions in which the triene system remains intact. Consistent with this interpretation, it has been found experimentally that $C_7H_7\cdot$ is an unreactive radical.[21]

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[14] The enthalpy of cleavage of biisopropyl (2,3-dimethylbutane) at 25° has been calculated from the heats of formation of biisopropyl (−42.49 kcal/mole) and the isopropyl radical (17.6 kcal/mole) [see "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953; P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964)].

[15] The heat of hydrogenation of bitropenyl at 25° in acetic acid is −138.8 kcal/mole which is just *twice* the heat of hydrogenation of cycloheptatriene, −70.5 kcal/mole [R. B. Turner, *et al., ibid.*, **79**, 4127 (1957)]. Our treatment of the $\pi$ system of bitropenyl as consisting of two noninteracting cycloheptatriene halves is consistent with this result.

[16] This reaction involves a hypothetical structure and should not be interpreted in a rigorous fashion.

[17] J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *ibid.*, **61**, 1868 (1939).

[18] R. B. Turner, *et al., ibid.*, **79**, 4127 (1957).

[19] These resonance energies are computed relative to a nonresonating model in which the heat of hydrogenation of cyclohexene is used for the first double bond, cycloheptene for the third, and an average of the two for the second. If the heat of hydrogenation of cycloheptene is employed for all three double bonds, one obtains 6.7 and 7.1 kcal/mole for the resonance energy in gas phase and solution, respectively. The use of these values rather than those cited in the text would not lead to a quantitatively significant modification of the total empirical RE of $C_7H_7\cdot$.

[20] The term "extra" resonance energy has been used previously in much the same way (see ref 4, p 243).

[21] F. R. Hunter, Ph.D. Thesis, University of Washington, 1966.

**Table II.** "Extra" Resonance Energies of Hydrocarbon Free Radicals

| Radical | "Extra" RE, kcal/mole | Ref |
|---|---|---|
| Cyclohexadienyl | 24[a] | *b*, *c* |
| Tropenyl | 21 | This work[d] |
| Triphenylmethyl | 16 | *e* |
| Pentadienyl | 15.4 | *c* |
| Benzyl | 12.5 | *f* |
| Allyl | 10.2 | *g* |

[a] This is an exceptionally high value for a "linearly" conjugated system. The significant increase relative to pentadienyl suggests that cyclohexadienyl is in fact a homocyclopentadienyl radical, in which cyclic delocalization occurs. [b] D. G. L. James and R. D. Stuart, *Chem. Commun.*, 484 (1966). [c] K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 241 (1966). [d] Benson and coworkers (footnotes *c*, *e–g*) use a definition of "extra" RE similar to that employed in this work. They take it to be the difference in bond dissociation energies between the CH bond in the unsaturated precursor to the radical and a similar CH bond in the parent saturated hydrocarbon. Since we are comparing our result to those obtained by these workers, we have applied their definition to the case of $C_7H_7\cdot$. The "extra" RE of tropenyl radical is given by $D(C_7H_7\text{–}H) - D((CH_3)_2CH\text{–}H)$. In footnote 24 we compute, using our experimental enthalpy of cleavage for bitropenyl, $D(C_7H_7\text{–}H) = 73.4$ kcal/mole. Since $D((CH_3)_2CH\text{–}H) = 94.5$ kcal/mole (footnote *e*), the "extra" RE is 21.1 kcal/mole in *excellent* agreement with the value obtained in the text (eq 10). [e] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). [f] R. Walsh, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 650 (1966). [g] D. M. Golden, A. S. Rodgers, and S. W. Benson, *ibid.*, **88**, 3196 (1966).

A comparison of the total empirical RE of $C_7H_7\cdot$ with an MO calculation of delocalization energy (DE) and with a VB resonance energy calculation is of interest. As has been pointed out previously,[4,5] such a comparison is not rigorously valid since the empirical RE incorporates changes in strain energy ($\sigma$-bond compression, bending, and torsion) and in $\sigma$-bond hybridization. It is conventional to circumvent this difficulty by choosing *empirical* values of the HMO parameter $\beta$ and the VB parameter $\alpha$ to give optimum agreement with the empirical resonance energies of a series of structurally similar compounds. One can then compare trends in the RE of related molecules with corresponding trends in the computed energies.

In this work we employ the values $\beta = -16.5$ kcal/mole and $\alpha = -30$ kcal/mole which have been obtained for a series of aromatic hydrocarbons.[4] The HMO DE of $C_7H_7\cdot$ is $2.54\beta$ which equals 42 kcal/mole, while the VB resonance energy is $1.08\alpha$ or 32 kcal/mole. Considering the approximate nature of the calculation, both of these values are in good agreement with the total empirical RE, 31 kcal/mole.

**Other Thermochemical Quantities.** A number of important thermochemical quantities, such as $\Delta H_f°(C_7H_7\cdot(g))$, $\Delta H_f°(C_7H_7^+(g))$, and $\text{RE}(C_7H_7^+)$, can readily be computed from $\Delta H°$ for the thermal cleavage of bitropenyl and data in the literature. In doing so we continue to make the approximation that the enthalpy of dissociation of neat liquid bitropenyl is the same as that in the gas phase.

The heat of formation of tropenyl radical is given by

$$\Delta H_f°(C_7H_7\cdot(g)) = \frac{1}{2}[\Delta H_f°(C_7H_7\text{–}C_7H_7(g)) + \Delta H°] \quad (11)$$

$\Delta H_f°(C_7H_7\text{–}C_7H_7(g))$ has been evaluated previously[12] using the Franklin group-equivalent method and $\Delta H_f°(C_7H_8) = 43.47$ kcal/mole;[22] the value obtained is 94.6 kcal/mole. From this and $\Delta H° = 35$ kcal/mole, we obtained $\Delta H_f°(C_7H_7\cdot(g)) = 64.8$ kcal/mole.[23,24]

This heat of formation can be used to compute the heat of formation of the tropenium ion. A number of attempts have been made to evaluate $\Delta H_f°(C_7H_7^+(g))$ because $C_7H_7^+$ is the prototype of the heptagonal aromatic system. The results obtained vary from 207 to 244 kcal/mole.[12,25] From $\Delta H_f°(C_7H_7\cdot(g)) = 64.8$ kcal/mole and a spectroscopic ionization potential for $C_7H_7\cdot$, $I_p = 6.237 \pm 0.01$ eV,[26] we compute $\Delta H_f°(C_7H_7^+(g)) = 209$ kcal/mole. This value is in excellent agreement with an estimate made from the appearance potentials of the benzyl halides, *i.e.*, 207–210 kcal/mole.[25,27]

Using this heat of formation, one can estimate the empirical RE of $C_7H_7^+$. By analogy with the treatment presented in the previous section for $C_7H_7\cdot$, the extra RE of $C_7H_7^+$ is given by

$$(\text{RE})_{\text{extra}} = \left|[\Delta H_f°(C_7H_7^+(g)) - \Delta H_f°(C_7H_8(g))] - [\Delta H_f°(i\text{-}C_3H_7^+(g)) - \Delta H_f°(C_3H_8(g))]\right| \quad (12)$$

Since $\Delta H_f°(C_3H_8) = -24.83$ kcal/mole,[15] $\Delta H_f°(C_7H_8) = 43.47$ kcal/mole,[22] and $\Delta H_f°(i\text{-}C_3H_7^+(g)) = 190$ kcal/mole,[28] $(\text{RE})_{\text{extra}} = 49$ kcal/mole. Adding to this the resonance energy of cycloheptriene (9 kcal/mole), we obtain 58 kcal/mole for the total empirical RE of $C_7H_7^+$. It is interesting to note that this value is considerably larger than the empirical RE of benzene (36 kcal/mole).

The resonance energy of $C_7H_7^+$ is much larger than that of $C_7H_7\cdot$, a result which is in accord with the fact that $C_7H_7^+$ satisfies the Hückel $4n + 2$ rule. The HMO theory correctly predicts a larger DE for $C_7H_7^+$ than for $C_7H_7\cdot$, *i.e.*, $2.99\beta$ (49 kcal/mole) *vs.* $2.54\beta$.

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(22) H. L. Fink, D. W. Scott, M. E. Cross, J. E. Messerly, and G. Waddington, *J. Am. Chem. Soc.*, 75, 2819 (1953).

(23) The value of $\Delta H_f°(C_7H_7\cdot(g))$ can be used in conjunction with the Franklin group-equivalent method to obtain another estimate of the "extra" resonance energy of $C_7H_7\cdot$. The heat of formation of II (Figure 1) is given by[21] $\Delta H_f°(\text{II}) = \Delta H_f°(C_7H_8(g)) + \Delta H_f°(\text{–}\dot{C}H\text{–}) - \Delta H_f°(\text{–}CH_2\text{–}) = 43.47 + 37.5 - 4.93 = 86.0$ kcal/mole. Since $\Delta H_f°(\text{I}) = 64.8$ kcal/mole, the "extra" RE equals 21.2 kcal/mole in excellent agreement with the value cited previously.

(24) The methylene CH bond dissociation energy of cycloheptatriene, $D(C_7H_7\text{–}H)$, can be estimated as follows: $D(C_7H_7\text{–}H) = \Delta H_f°(C_7H_7\cdot(g)) + \Delta H_f°(H\cdot(g)) - \Delta H_f°(C_7H_8(g)) = 64.8 + 52.1 - 43.5 = 73.4$ kcal/mole.

(25) (a) F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 1489 (1954); (b) F. H. Field and J. L. Franklin, *ibid.*, **22**, 1895 (1954); (c) S. Meyerson and P. N. Rylander, *ibid.*, **27**, 901 (1957); (d) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); (e) S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCullum, *ibid.*, **81**, 2606 (1959); (f) R. B. Turner, H. Prinzbach, and W. von E. Doering, *ibid.*, **82**, 3451 (1960); (g) K. R. Jennings and J. H. Futtrell, *J. Chem. Phys.*, **44**, 4315 (1966).

(26) (a) B. A. Thrush and J. L. Zwolenik, *Discussions Faraday Soc.*, **35**, 196 (1963). (b) This value has been confirmed by F. A. Elder and A. C. Parr (private communication) using photoionization techniques.

(27) (a) It should be noted that, using different thermochemical values, Turner, Prinzbach and Doering[25f] have employed the appearance potential of benzyl bromide (ref 25e) to obtain a slightly higher value, $\Delta H_f°(C_7H_7^+(g)) = 216.3 \pm 1.2$ kcal/mole. (b) The higher range of values, *i.e.*, 230–240 kcal/mole, was obtained from appearance potentials of hydrocarbons. The discrepancy is most probably due to appreciable excess energy in the products of the ionization process for the hydrocarbons but not for the benzyl halides (F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 80).

(28) F. H. Field and J. L. Franklin, ref 27, p 260.

## Experimental Section

The esr spectrometer employed, the apparatus used to generate elevated temperatures and to measure the sample temperature, and the sample preparation technique have been described elsewhere.[6c,d]

Purification of the bitropenyl used in this work was accomplished by column chromatography (Merck alumina) using *n*-pentane as eluent, followed by recrystallization from *n*-pentane and then sublimation.

An approximate measurement of the density of bitropenyl as a function of temperature was required for the analysis leading to $\Delta H^\circ$ and was therefore made. A known weight of bitropenyl was added to a section of a graduated 1-ml pipet which was sealed at one end. The volume of the bitropenyl was measured at various temperatures in the range 80–140°.

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# Chemical Ionization Mass Spectrometry. IX. Temperature and Pressure Studies with Benzyl Acetate and *t*-Amyl Acetate

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**Abstract:** The chemical ionization mass spectra of benzyl acetate and *t*-amyl acetate have been determined as a function of the mass spectrometer ionization chamber temperature and the pressure in the ionization chamber of the esters. Most of the runs were made using $i\text{-}C_4H_{10}$ as reactant, but some measurements were made using $CH_4$ as reactant. The results obtained in the study are the following. (A) As a check on the apparatus and method, measurements were made of the $H(H_2O)_2^+\text{–}H(H_2O)_3^+$, $H(H_2O)_3^+\text{–}H(H_2O)_4^+$, and $H(H_2O)_4^+\text{–}H(H_2O)_5^+$ equilibria in the gaseous water ionic system. Thermodynamic values in good agreement with the results of Kebarle, *et al.*,[9] were obtained for 3,4 and 4,5 equilibria. (B) Ion intensities in $i\text{-}C_4H_{10}$ are presented for pressures of $i\text{-}C_4H_{10}$ between 0 and 1.0 Torr. At pressures above about 0.6 Torr, $t\text{-}C_4H_9^+$ comprises about 95% of the total ionization of the compound. (C) Mass spectra of the two esters with $i\text{-}C_4H_{10}$ as reactant are given at low, intermediate, and high source temperatures. The spectra of benzyl acetate using $CH_4$ as reactant is given at two temperatures. Extensive changes in the spectra occur as the temperature is changed when $i\text{-}C_4H_{10}$ is reactant. Several equilibria are observed at lower temperatures, and extensive amounts of dissociation occurs at high temperatures. With $CH_4$ as reactant extensive dissociation is observed at both temperatures studied. (D) Residence times under chemical ionization conditions (reactant = $i\text{-}C_4H_{10}$, $P_s = 0.70$ Torr) are calculated and tabulated for the several ions investigated. An equation for calculating rate constants for unimolecular ionic decompositions occurring under chemical ionization conditions is given. (E) Rate constants for the formation of benzyl ion and *t*-amyl ion from protonated benzyl acetate and protonated *t*-amyl acetate determined at various temperatures. The activation energies and log *A* values for benzyl ion production are 12.3 kcal/mole and 11.2, and for production of *t*-amyl ion the values are 12.4 kcal/mole and 12.4. The relative magnitudes of the activation energies are tentatively identified with the relative energies of the charged centers in the carbonium ions, and it is suggested that the technique may comprise a useful new method for obtaining relative energies of gaseous ions. The lower *A* factor for the formation of benzyl ion is rationalized in terms of the postulate of the formation of a torsional vibration in the $C_6H_5\text{–}CH_2$ bond in the transition state of the reaction. (F) Equilibrium reactions are observed in the formation of the following ions: the protonated dimers of the two esters, the association complexes between the protonated ester molecules and residual water in the mass spectrometer, and the association complex between benzyl acetate and $C_3H_3^+$. The usual thermodynamic quantities are calculated from the equilibria. The entropies obtained for all these reactions are much higher than would be expected for association reactions, and the entropy change for the formation of the protonated dimer of benzyl acetate has the astonishingly high value of +14 eu. (G) The effect of repeller voltage on the chemical ionization spectrum of benzyl acetate was investigated. Dissociation processes increase with increasing repeller voltage, but one finds that a tenfold increase in repeller voltage has about the same effect in increasing the benzyl ion intensity as a 10% increase in temperature. (H) The pressure of benzyl acetate in the ionization chamber was varied, and a rate constant for the over-all reaction of ions from $i\text{-}C_4H_{10}$ with benzyl acetate was determined. Investigations were made at two temperatures (99 and 178°). The values obtained are $5.1 \times 10^{-9}$ (99°) and $3.2 \times 10^{-9}$ cc/(mol sec) (178°). These values are in reasonable agreement with theoretical values which can be calculated for ion–permanent dipole reactions. (I) Rate constants for the total reaction of ions from $i\text{-}C_4H_{10}$ and $CH_4$ with the two esters at various temperatures have been determined. A strong negative temperature coefficient for the rate constant obtained in the $i\text{-}C_4H_{10}$–benzyl acetate system is observed, and extraordinarily large values of the rate constants are observed for all the systems.

We have observed that the temperature of the ion source can have a profound effect upon the chemical ionization mass spectra of substances, and this paper is a report of a study of the phenomenon. We also include the results of pressure studies which were carried out in conjunction with the temperature studies. The compounds investigated were benzyl acetate and *t*-amyl acetate, and the reactant gases were isobutane and methane.

The effect of temperature upon electron impact mass