demonstrates the concerted nature of the process and is in agreement with the values generally observed for this type of reaction (compare ref 1 and Table II). The B conformation of the 7-methyl-1,3,5-cycloheptatriene favors the 1,5 hydrogen transfer. It is not surprising therefore that the activation energy observed for this cyclic 1,3-diene is similar to that previously reported for cisoid linear compounds. It can be concluded that no more than 1–2 kcal of extra strain is introduced into the bicyclic transition complex, unless some of the strain energy is compensated by a basically lower activation energy for hydrogen transfer in the 7-MCHT as compared to open-chain compounds.[2] There is, however, no evidence that would warrant this assumption.

The cyclic six-center transition complex is shown in scheme B by a static representation of a dynamic resonance system, involving three-electron and one-electron bonds, respectively.[26] The flattened carbon skeleton of the six-membered transition complex would introduce some additional strain into the molecule. Since complete flattening of the cycloheptatriene molecule requires an activation energy of about 6 kcal,[24b] 1 to 2 kcal of extra strain would appear to be reasonable. It is interesting to note that the additional double bond in the 7-MCHT which is not directly involved in the six-center transition complex has no measurable effect on the activation energy of the process.[27] The additional double bond, conjugated onto the transition complex, is not in the same plane with the transition ring and therefore has no stabilizing effect on the latter.

In general, the activation energies for 1,5 hydrogen transfer are not sensitive to changes in the substituents of the basic cisoid structure of the molecule.[1] Acyclic and cyclic systems, as well as 1,3-diene and the corresponding vinylcyclopropane systems, require closely the same activation energies, and the ring size seems to be of little influence.[1] The only exception to this general insensitivity of the reaction rates for the concerted 1,5 hydrogen transfer are the unusually low activation energies of about 23 kcal, observed for the positional isomerization in cyclopentadiene systems[7,23] (liquid phase). The thermal rearrangement in these systems appears to proceed *via* a 1,5 hydrogen transfer also.[17,23,28] The difference of nearly 10 kcal in activation energy when compared with the values for 1,5 shifts in other systems has been attributed to the unique structure and molecular orbital pattern of the ground-state cyclopentadiene.[1] Benson, *et al.*,[29] recently proposed that the pyrolysis of 1,3-cycloheptadiene involves a complex radical reaction mechanism with pseudo-unimolecular kinetics. The over-all activation energy is 41 ± 4 kcal mole^{-1}. It is conceivable that such radical reactions, initiated by the disproportionation of two diene molecules into a monoolefinic and diolefinic radical, might compete with the 1,5 hydrogen shift in some 1,3-dienes.

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(26) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 241 (1966).

(27) In agreement with this, liquid-phase studies have shown that the rate constants for 1,5 hydrogen transfer in substituted cycloheptatrienes were not significantly affected by phenyl substituents.[6]

(28) V. A. Miranov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

(29) S. W. Benson and R. Shaw, *J. Am. Chem. Soc.*, in press.

Free Radicals by Mass Spectrometry. XXXVI. Ionization Potentials of Conjugated and Nonconjugated Radicals

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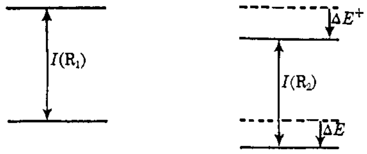
Contribution N.R.C. No. 9629 from the Division of Pure Chemistry,
National Research Council, Ottawa, Canada. *Received January 30, 1967*

Abstract: The ionization potentials of several free radicals have been measured by electron impact: 3-cyclopentenyl, 7.54 v; acyclic pentadienyl, 7.76 v; ethylallyl, 7.65 v; 3-cyclohexenyl, 7.54 v; and 4-cyclohexenyl, 7.54 v. A comparison of allylic and corresponding nonallylic radicals shows no significant difference in ionization potential. Stabilization of the ground state of the former by π-electron delocalization is evidently paralleled by that in the cation. From appearance potentials, $\Delta H_f(\text{cyclo-}C_5H_7^+) = 211$ kcal/mole and $\Delta H_f(\text{cyclo-}C_5H_7) = 37$ kcal/mole can be estimated.

The effects of structural differences on the ionization potentials of free radicals has been reviewed recently[3] with respect to both the semiempirical molecular orbital method and the resonance treatment. The ionization potential, defined as the difference in energy between the ground state of the neutral radical and the lowest energy state of the cation, is a direct measure of the relative degree of stabilization in these levels, in the neutral radical by electron delocalization (ΔE) and in the cation by charge delocalization (ΔE^+).



A comparison of ionization potential differences in closely related radicals is therefore of value in interpreting the magnitude of such effects.

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(1) NATO Fellow, 1965–1966.

(2) Canada Council Fellow, 1966.

(3) A. Streitwieser, Jr., *Progr. Phys. Org. Chem.*, 1, 1 (1963).

For some structural changes, such as those brought about by substitution of alkyl groups around a carbon atom, ΔE is relatively small, a few kilocalories/mole, but ΔE^+ is large, usually considered to be a result of hyperconjugation. Along the series methyl, ethyl, isopropyl, *t*-butyl, then, a very rapid decrease in ionization potential occurs, nearly 3 v in all. A similar decrease, although less rapid, is brought about by increasing size in odd-alternate hydrocarbon radicals, for example, allyl, benzyl, naphthylmethyl, diphenylmethyl. The experimentally observed electron-impact ionization potentials show a decrease in quantitative agreement[4] with calculations[5-7] based on a model which takes account of the effect on electron repulsions of a spreading out of the nonbonding orbital. In all these cases the stabilization or resonance energy in the cation is greater than that in the neutral species.

The situation is less clear when one considers changes in ΔE and ΔE^+ resulting from the introduction of possibilities for allylic resonance into the radical, and its cation, without appreciably altering its size. In this case the neutral radical is already stabilized appreciably, by about 0.5 v[8] or possibly more[9,10] by electron delocalization, an effect much greater than can be achieved by hyperconjugational effects in a neutral species. Should we then expect the allylic ion to have, or not have, a further additional stabilization over and above that for the corresponding nonallylic ion? If it does not have, the ionization potential of the allylic radical will be increased over that of its nonallylic counterpart by the electron delocalization in the neutral species. This question has been the subject of some discussion.[11]

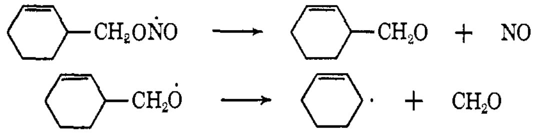
Existing experimental data do not provide sufficient allylic–nonallylic pairs of radicals of corresponding size from which to make a comparison. In the present work the ionization potentials of a number of unsaturated hydrocarbon radicals have been measured for comparison with corresponding saturated or nonallylic radicals measured earlier by the same method.

Experimental Section

The radicals were generated by thermal decomposition of suitable derivatives in a reactor attached to a mass spectrometer. This apparatus and the method of evaluating the appearance potentials have been described.[12]

3-Cyclopentenyl Radical. The radical was generated by the thermal decomposition of 3,3′-bicyclopentenyl. This was prepared[13] through 3-chlorocyclopentene and the Grignard reagent and purified by low-pressure distillation. The 3,3′-bicyclopentenyl decomposed at a furnace temperature of about 600°. The mass 67 peak at low electron energies showed a substantial increase starting at 600°, a maximum at 720°, with a rapid decrease above this temperature resulting from decomposition of the radical to an H atom and cyclopentadiene. The latter was identified by features of its mass spectrum and by a comparison of its ionization potential with that of an authentic sample. This confirmation of the decomposition product shows that the radical was indeed cyclopentenyl and not the linear dienyl radical.

3-Cyclohexenyl Radical. The radical was obtained by the thermal decomposition of 3-cyclohexenylmethyl nitrite, which was prepared from the corresponding carbinol[14] by the action of dilute H_2SO_4 and $NaNO_2$. The decomposition of the nitrite followed the sequence[15]

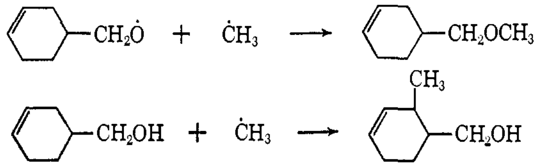

(1)
(2)

The increase in the mass 81 peak due to the radical and its decomposition to form 1,3-cyclohexadiene are shown in Figure 1. The latter product was identified by its ionization potential of 8.54 v, compared with 8.54 v for 1,3-cyclohexadiene and 9.05 v for 1,4-cyclohexadiene, measured in separate experiments. At furnace temperatures above those shown in Figure 1, the mass 80 peak decreased and a mass 78 peak (benzene) appeared. This sequence shows that the radical at mass 81 was 3-cyclohexenyl.

4-Cyclohexenyl Radical. The preparation of this radical from 4-cyclohexenylmethyl nitrite through reactions 1 and 2 was less straightforward, owing to its nonallylic structure and the greater activation energy necessary for reaction 2. The unusually high thermal stability observed for the presumed alkoxy radical at mass 111 suggested that in addition to bond rupture as in (2), an isomerization was taking place.


(3)

This assumption was tested by "titrating" the radical of mass 111 with CH_3 radicals produced simultaneously by thermal decomposition of ethyl nitrite. A peak at mass 108 was produced, but no significant increase was produced at the parent mass of the addition compound, mass 126. The two possible addition compounds are


(4)
(5)

The mass spectra of these two products are not known, but by comparison with analogous compounds it is clear that cyclohexenyl methyl ether would have a substantial parent ion intensity and no peak at mass 108. The alcohol, on the other hand, would have a small parent ion intensity and a large peak at mass 108, corresponding to loss of H_2O from the parent ion. Titration with C_2H_5 radicals from *n*-propyl nitrite gave a similar result: no peak at mass 140, but a substantial peak at mass 122. It seems fairly certain, therefore, that rearrangement by reaction 3 at 350–400° is competitive with dissociation by the analog of reaction 2.

At temperatures of 400° and above, formation of the 4-cyclohexenyl radical was observed, although the yield was not high. Using low-energy electrons, the mass 81 peak increased with furnace temperature up to 550°, then decreased, becoming nearly zero at 850°. The same trend was followed by three small peaks: 162 (81 + 81), 192 (81 + 111), and 174 (192 − 18). In experiments with CH_3 radical addition the formation of peaks at mass 96 (methylcyclohexene) and its fragment ion at mass 68 (loss of 28) was observed. At the lower furnace temperatures (375°) the mass 68/96 ratio of this addition product was close to that of 4-methylcyclohexene. As the furnace temperature was increased, the 68/96 ratio changed gradually to a value closer to that of 3-methylcyclohexene. This change in peak ratio, shown in Figure 2, strongly suggests that the 4-cyclohexenyl radical isomerizes at higher temperatures to the 3-cyclohexenyl radical. The ionization potential of the radical measured at intervals over this temperature range showed, however, no detectable change. At 850° the product of

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[4] A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 1052 (1960).

[5] N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

[6] A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

[7] S. Ehrenson, *J. Phys. Chem.*, **66**, 706 (1962).

[8] K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964); D. M. Golden, A. S. Rodgers, and S. W. Benson, *ibid.*, **88**, 3196 (1966).

[9] J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 6652 (1965).

[10] J. B. Homer and F. P. Lossing, *Can. J. Chem.*, **44**, 2211 (1966).

[11] J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **19**, 1073 (1951); J. Halpern, *ibid.*, **20**, 744 (1952); J. L. Franklin and H. E. Lumpkin, *ibid.*, **20**, 745 (1952).

[12] R. Taubert and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 1523 (1962).

[13] K. S. Sidhu, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **44**, 531 (1966).

[14] A. T. Blomquist, J. Verdol, C. L. Adami, J. Wolensky, and D. D. Phillips, *J. Am. Chem. Soc.*, **79**, 4976 (1957).

[15] F. P. Lossing and J. B. de Sousa, *ibid.*, **81**, 281 (1959).

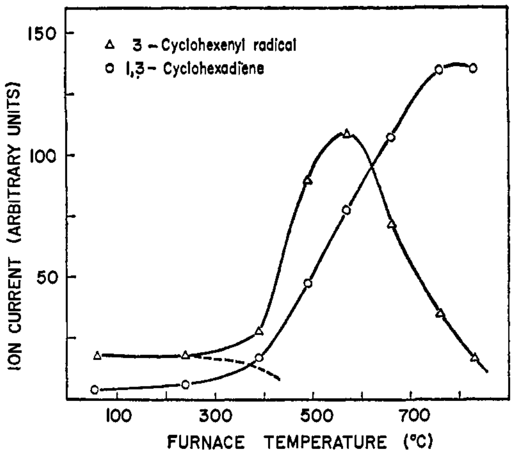

Figure 1. The formation and decomposition of 3-cyclohexenyl radical as a function of furnace temperature, shown by the mass 81 peak at low electron energies. The ion current at mass 81 below 300° represents the "tail" of the ionization efficiency curve for the 81^+ fragment ion from the undissociated nitrite. The dotted line shows approximately the decrease in this contribution to the 81^+ peak with increasing temperature. The rise shown for 1,3-cyclohexadiene (mass 80) is followed by a decrease above 800°, with formation of benzene.

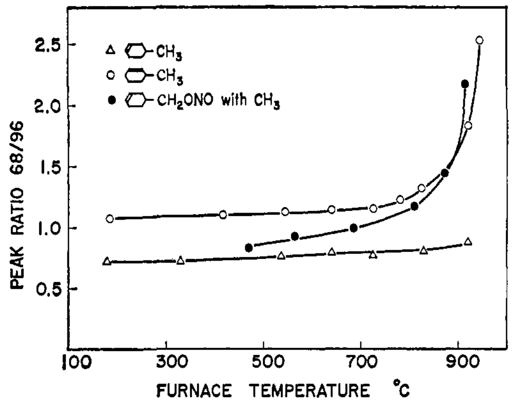

Figure 2. Isomerization of 4-cyclohexenyl radical to 3-cyclohexenyl radical. The peak ratio 68/96 for the product of CH_3 addition to the radical is compared with the ratios for pure samples of 4-methylcyclohexene and 3-methylcyclohexene, under the same temperature conditions. It can be seen that there is no isomerization of the pure compounds, but the peak ratio for the CH_3 addition compound changes from close to that for 4-methylcyclohexene at low temperatures to that of 3-methylcyclohexene at high temperatures. The sharp increase in ratio above 850° is caused by the products of decomposition of 3-methylcyclohexene. By contrast, 4-methylcyclohexene is stable at 900°.

mass 80 arising from decomposition of the radical had an ionization potential of 8.6 v, corresponding to 1,3-cyclohexdiene (8.5 v) rather than 1,4-cyclohexadiene (9.05 v).

Cyclohexadienyl Radical. This radical was generated, although in extremely poor yield, from the thermal decomposition of cyclohexadienylmethyl nitrite. The nitrite was obtained from a sample of cyclohexadienylcarbinol prepared following the procedure of Pleininger, *et al.*[16] The addition of CH_3 radicals to the reaction stream at 510° gave a product of mass 94, methylcyclohexadiene. Most of the radicals, however, were decomposed to benzene, and at all temperatures the quantity of radicals was too small to permit measurement of the ionization potential in the present apparatus.

Pentenyl Radical. The $CH_3CH_2CH{=}CH\dot{C}H_2$ radical was generated from $CH_3CH_2CH{=}CHCH_2CH_2ONO$, prepared from the commerically available alcohol. The radical yield was a maximum at 500°. Titration with CH_3 radicals and with phenyl radicals (from the simultaneous pyrolysis of *t*-butyl perbenzoate) gave peaks for the appropriate addition products at masses 84 and 146, respectively. Addition to this radical at both the 1 and 3 allylic positions presumably occurred. At higher furnace temperatures the radical decomposed by both H loss and CH_3 loss

$$CH_3CH_2CH{=}CH\dot{C}H_2 \longrightarrow H + CH_3CH{=}CHCH{=}CH_2 \quad (6)$$

$$\longrightarrow CH_3 + CH_2{=}CHCH{=}CH_2 \quad (7)$$

Pentadienyl Radical. This radical was produced from pyrolysis of the bromide, which was obtained in poor yield from 1,4-pentadiene and N-bromosuccinimide in CCl_4 solution with benzoyl peroxide as a catalyst. Although a freshly prepared sample of the bromide gave a good yield of pentadienyl radical without complications, samples which had stood for some hours at room temperature gave on pyrolysis the cyclopentenyl radical as well as the pentadienyl radical, as shown by an inflection in the radical ionization efficiency curve. A slow cyclization of the bromide, which is presumably initially a mixture of 3-bromo-1,4-pentadiene and 5-bromo-1,3-pentadiene, must occur at room temperature. From a freshly prepared sample of bromide, the radical yield was a maximum at 720°. Above this temperature decomposition of the radical became quite rapid, but the identity of the products was not established.

Results and Discussion

The ionization potentials of the unsaturated radicals are given in Table I, together with values for corresponding saturated radicals previously measured by the same method. A striking feature is the remarkably small difference in ionization potential, not only between the various unsaturated radicals, but between these and the saturated homologs. The differences between the true adiabatic ionization potentials of the two types of radical may indeed be even smaller. It should be noted that the potentials measured by the method employed here refer almost certainly to formation of ions with some excitational energy. Photon-impact[17] and retarding potential difference (RPD) electron-impact[18] measurements on noncyclic alkyl radicals gave ionization thresholds 0.3–0.5 v lower than those obtained by the conventional method. The RPD electron-impact curves for the alkyl radicals[18] show a low probability for the transition of lowest energy, followed by a steeper rise a few tenths of a volt higher, presumably corresponding to a second ionization potential.[19] With the conventional method this first transition cannot be observed because of low-energy resolution. For olefinic molecules the difference between the photoionization or spectroscopic values and the electron-impact values is generally smaller, 0.2 v or less[20] (see also Table II). For this reason it seems likely that the adiabatic ionization potentials of the unsaturated radicals are not lower than those of the saturated counterparts, but that both are in the region of 7.3–7.4 v.

Even without this reservation, the present data show that the increased stability of the neutral allylic radicals over that of the nonallylic radicals, 0.5 v or possibly more, is paralleled by a corresponding increase in the stabilization of allylic cations. Possibly the best illustration of this point is provided by the identity of the measured ionization potential for the allylic 3-cyclohexenyl radical and the nonallylic 4-cyclohexenyl radical.

In this regard it is significant that the ionization potential of the pentadienyl radical is higher than those of the monounsaturated radicals. The value observed

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[16] A. Pleininger and G. Ege, *Chem. Ber.*, **94**, 2088 (1961).

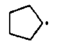
[17] F. A. Elder, C. Giese, B. Steiner, and M. Inghram, *J. Chem. Phys.*, **36**, 3292 (1962).

[18] C. E. Melton and W. H. Hamill, *ibid.*, **41**, 3464 (1964).

[19] C. E. Melton and H. W. Joy, *ibid.*, **42**, 1986 (1965).

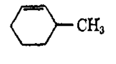
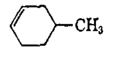
[20] J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **81**, 2064 (1959).

Table I. Ionization Potentials of Saturated and Unsaturated Radicals

Unsaturated radical	Ionization potential, v This work	Lit.	Saturated radical	Ionization potential, v
	7.54	...		7.79[a]
	7.54	...		7.76[a]
	7.54	...	...	...
$CH_2{=}CH\dot{C}HCH{=}CH_2$	7.76	7.73[b]	$CH_3CH_2\dot{C}HCH_2CH_3$	7.86[c]
$CH_3CH_2\dot{C}HCH{=}CH_2$	7.65	...	...	...
$CH_3\dot{C}HCH{=}CH_2$	...	7.71[d]		

[a] R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961). [b] Reference 21. [c] Reference 12. [d] Reference 23.

Table II. Ionization Potentials of Molecules

Compound	Ionization potential, v This work	Lit.	Method for lit. values
	9.08	...	
	9.13	8.91[a]	Photoionization
	8.54	8.40[b]	Ultraviolet spectroscopy
	9.05	...	

[a] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962). [b] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), **A179**, 201 (1941).

here is in good agreement with an earlier value.[21] The stabilization energy of the acyclic dienyl radical has been shown[22] to be appreciably greater than that of a monoallylic radical, although not twice as great. This extra stabilization of the neutral radical seems not to be available to the cation.

The small decrease in ionization potential on going from the methylallyl radical (7.71 v)[23] to the ethylallyl radical (7.65 v) is in line with that expected for substitution at an "unstarred" carbon atom. Correspondingly, the decrease from cyclopentenyl to cyclohexenyl radical is evidently smaller than the reproducibility of the present measurements (±0.1 v).

Appearance Potentials of $C_5H_7^+$ Ions. The appearance potentials for $C_5H_7^+$ from cyclopentene, 3-methylcyclopentene, 3-methyl-1,4-pentadiene, and 3,3′-bicyclopentenyl are given in Table III. Excluding the latter for the moment, the appearance potentials together with the relevant heats of formation (see Appendix) lead in good agreement to $\Delta H_f(C_5H_7^+) = 211$ kcal/mole. Current thermochemical data would suggest that this value is much too low to correspond to an acyclic $C_5H_7^+$ ion. The isomerization is about 14

$$\longrightarrow CH_2{=}CH\overset{+}{C}HCH{=}CH_2 \qquad (8)$$

kcal/mole endothermic,[22] and the increase in ionization potential is a further 5 kcal/mole. Taking the dienyl resonance energy to be 15.4 kcal/mole,[22] one can compute ΔH_f for the acyclic pentadienyl radical as follows. If $D(sec\text{-}C_5H_{11}\text{–}H) - D(\text{acyclic-}C_5H_7\text{–}H) = 15.4$ kcal/mole and the former is 94.6 kcal/mole,[24] the latter becomes 79.2 kcal/mole. From ΔH_f(1,4-pentadiene) = 25.20 kcal/mole,[25] $\Delta H_f(\text{acyclic-}C_5H_7)$ becomes 52.3 kcal/mole. Adding $I(\text{acyclic-}C_5H_7) = 7.76$ v, one obtains $\Delta H_f(\text{acyclic-}C_5H_7^+) = 231$ kcal/mole. This is 20 kcal higher than the observed value. On these grounds the threshold for $C_5H_7^+$ from these derivatives would be too low to correspond to formation of acyclic $C_5H_7^+$. In view of the uncertainties in appearance potential data this conclusion cannot be a firm one; nevertheless, it seems probable that the derived energy should be taken as that of the cyclic ion even in the case of 3-methyl-1,4-pentadiene. The existing evidence for such cyclization and decyclization of isomeric ions has been discussed recently.[26] Taking 211 kcal/mole for $\Delta H_f(\text{cyclo-}C_5H_7^+)$ and subtracting $I(\text{cyclo-}C_5H_7) = 7.54$ v, one gets $\Delta H_f(\text{cyclo-}C_5H_7) = 37$ kcal/mole. Although some cancellation of errors will occur in deriving this value since $A(C_5H_7^+)$ and $I(C_5H_7)$ are both upper limits, a reliable estimate of the possible error in this heat of formation cannot be made. From this value D(3-cyclopentenyl-H) = 81 kcal/mole.

Table III. Appearance Potentials (A) and ΔH_f for cyclo-$C_5H_7^+$ Ion

Compound	Fragments	$A(C_5H_7^+)$, v	$\Delta H_f(C_5H_7^+)$, kcal/mole	
Cyclopentene	$C_5H_7^+ + H$	11.19	214	Av 211
3-Methylcyclopentene	$C_5H_7^+ + CH_3$	10.52	210	
3-Methyl-1,4-pentadiene	$C_5H_7^+ + CH_3$	9.77	210	
3,3′-Bicyclopentenyl	$C_5H_7^+ + C_5H_7$	9.75	$\Delta H_f(R^+) + \Delta H_f(R) = 249$	

The appearance potential for $C_5H_7^+$ from 3,3′-bicyclopentenyl provides an independent check on the internal consistency of the A and I values, since both

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(21) D. P. Stevenson, private communication, cited in ref 3.

(22) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 241 (1966).

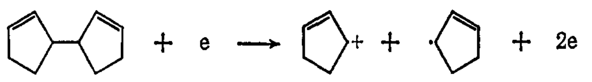
(23) C. A. McDowell, F. P. Lossing, I. H. S. Henderson, and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1956).

(24) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(25) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh Pa., 1953.

(26) A. G. Harrison in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Interscience Publishers, New York, N. Y., in press.

$C_5H_7^+$ and neutral C_5H_7 are formed. From $A(C_5H_7^+)$ for the process


(9)

and the relationships

$$A(R^+)_{RR} = \Delta H_f(R^+) + \Delta H_f(R) - \Delta H_f(RR)$$

and

$$I(R) = \Delta H_f(R^+) - \Delta H_f(R)$$

one can derive

$$I(R) = 2\Delta H_f(R^+) - \Delta H_f(RR) - A(R^+)_{RR} = 7.50 \text{ v}$$

This is in good agreement with the directly measured value of 7.54 v. It would appear that both the ionic and neutral fragments in (9) have retained the cyclic structure.

Appendix

ΔH_f(3-methyl-1,4-pentadiene) was calculated to be 18.3 kcal/mole from standard data[25] for isobutane and 3-methyl-1-butene, using the method of Benson and Buss.[27] ΔH_f(3-methylcyclopentene) = 1.0 kcal/mole was calculated from ΔH_f(cyclopentene) = 7.87 kcal/mole[25] by comparison with the increment resulting from substituting CH_3 for H in comparable positions (ΔH_f(methylcyclopentane) − ΔH_f(cyclopentane) = −7.0 kcal/mole, ΔH_f(3-methyl 1-butene) − ΔH_f(1-butene) = −6.9 kcal/mole). ΔH_f(3,3′-bicyclopentenyl) was estimated in two ways: a group equivalent method[28] from cyclopentene and 3-methylcyclopentene gave 24.8 kcal/mole, and a comparison with the analogous change from propylene to 1,5 hexadiene gave 23.2 kcal/mole. The average, 24 kcal/mole, is probably correct to within ± 2 kcal/mole. As recommended recently,[24] $\Delta H_f(CH_3)$ was taken to be 34 kcal/mole[29] rather than the earlier value of 32.5 kcal/mole.

(27) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).
(28) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).
(29) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965).

Mean Activity Coefficient of Polyelectrolytes in the Ternary System Water–Sodium Polyacrylate–Sodium Chloride

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Abstract: Isopiestic vapor pressure measurements were carried out for the ternary system water–sodium polyacrylate–sodium chloride. The variation of the isopiestic ratio with the concentration fraction of an electrolyte component is generally much more pronounced in the water-polyelectrolyte–simple electrolyte system than it is in the water–simple electrolyte–simple electrolyte system. The mean activity coefficients of sodium polyacrylate and sodium chloride are obtained as functions of the concentrations of the two components. From these data, interaction parameters between polyelectrolyte and polyelectrolyte, polyelectrolyte and simple electrolyte, and simple electrolyte and simple electrolyte are obtained as a function of the polyelectrolyte concentration. The magnitude of the polyelectrolyte–polyelectrolyte interaction parameter is much larger than other parameters obtained at zero polymer concentration. The second virial coefficient of the polyelectrolyte is calculated from these interaction parameters and is in good agreement with data from other measurements.

In some previous papers from this laboratory, the mean activity coefficients of polyelectrolytes in the binary systems water–polyelectrolyte were determined by emf measurements of a concentration cell with transference[2-4] and isopiestic vapor pressure measurements.[5] These studies have revealed that the contribution of macroions to the thermodynamic properties of polyelectrolyte solutions is unexpectedly large, and a somewhat regular distribution of electric charges in the solutions can be set up by an intermacroion "linkage" through the intermediary of gegenions. Although these conclusions are important, it has been impossible to compare successfully these experimental data obtained for the mean activity coefficients with those obtained by other methods, since the experiments so far reported from other laboratories, from which the mean activity coefficient data can be derived, were mostly performed not in binary systems but in ternary systems water–polyelectrolyte–simple electrolyte. It was interesting, therefore, to extend our measurements to the ternary systems. The knowledge of these solutions, furthermore, is doubtlessly indispensable to the understanding of naturally occurring biological systems. In the present paper, the mean activity coefficients of sodium polyacrylate (NaPAA) and sodium chloride in water–NaPAA–NaCl are determined by isopiestic vapor pressure measurements. These data are compared with those of binary solutions water–

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