at 25°. In the present study, as a wall reaction the exchange may have proceeded at the observed slow rate even at room temperature. This explanation would take into account the lack of any change in the isotopic composition of the oxygen in the thermal reaction.

Since oxygen in a homogeneous gaseous system is an extremely effective scavenger of free radicals, it is unlikely that the photochemical formation of acetone-O^{18} is through a synthesis from radical fragments, *e.g.*, CH_3 and CH_3CO^{18}. Acetone-O^{18} must be formed by an exchange process between an acetone molecule and an oxygen^{18} bearing molecule or radical. The present study does not allow one to decide unequivocally on the nature of the reactants in this reaction. Three possibilities may be considered. In the order of increasing likelihood, these are

(i) $$CH_3COCH_3^* + H_2O^{18} \longrightarrow CH_3CO^{18}CH_3 + H_2O \quad (2)$$

The asterisk denotes a photochemically excited molecule. This reaction is akin to the thermal exchange process but may proceed more rapidly under the same conditions due to the photoenergy available.[5] But since H_2O^{18} is built up in the system only as the photo-oxidation proceeds, (2) will have to compete unfavorably with either the deactivation of the excited ketone molecule by oxygen, or its reaction with oxygen. At least for the triplet state, this is believed to be an extremely efficient reaction. At high oxygen pressure no difference may be seen in the rates of formation of acetone-O^{18} between 0.6% and 2.5% conversions. Hence the build-up of H_2O^{18} (or any other product) does not seem to control the reaction.

(ii) The second possibility is a reaction such as

$$CH_3COCH_3 + RO\cdot^{18} \longrightarrow CH_3CO^{18}CH_3 + RO \quad (3)$$

The radical $RO\cdot^{18}$ may be any of the several oxygen containing intermediates in the oxidation of acetone. The most important criterion is that reaction 3 may not be followed by any step in which the radical $RO\cdot$ gives rise to molecular oxygen, as this would lead to a change in the isotopic composition of the molecular oxygen. It is not obvious which radical species would be likely to take part in (3) and also fulfill the condition mentioned above. From the experiment on 3-pentanone:azoethane:O_2^{18}, it may be concluded that introduction of ethyl radicals into the system by the photolysis of azoethane is not sufficient to lead to the formation of 3-pentanone-O^{18}.

(iii) A third possibility is the reaction

$$CH_3COCH_3^* + O^{18}{}_2 \longrightarrow \text{complex} \quad (4)$$

$$\text{complex} + CH_3COCH_3 \longrightarrow \left\{\begin{matrix} CH_3CO^{18}CH_3 \\ \text{or} \\ CH_3COCH_3 \end{matrix}\right\} + \text{oxidation intermediates} \quad (5)$$

The reverse of (4) is postulated to be slow and not to result in an exchange of oxygen atoms, while (5) may be a rapid reaction. This reaction scheme, although vague, is capable of explaining the observations. It would not predict a dependence on the intensity, or oxygen pressure (for moderate pressures), which are as observed. It would also predict that the photochemical formation of an O^{18}-ketone may be a general reaction for this class of compounds.

This scheme further suggests that there is a relationship between the formation of acetone-O^{18} and the photo-oxidation process. Hence useful information concerning the two processes may be obtained only by a simultaneous quantitative study of the oxidation products along with the labelled ketone.

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[5] It has been observed in this Laboratory that at 3130 Å. a mixture of acetone and D_2O vapor does not give rise to acetone-*d* or acetone-d_2 photochemically in detectable amounts. This suggests that any photoexchange process would involve only an oxygen atom and not a –OH group.

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Free Radicals by Mass Spectrometry. XX. Ionization Potentials of Cyclopentadienyl and Cycloheptatrienyl Radicals

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The cyclic free radicals, cyclopentadienyl ($C_5H_5\cdot$) and cycloheptatrienyl (tropenyl) ($C_7H_7\cdot$), have been produced by pyrolytic reactions and identified by mass spectrometry. By electron impact the ionization potentials are found to be: cyclopentadienyl 8.69 ± 0.1 and cycloheptatrienyl 6.60 ± 0.1 v. From thermal and appearance potential data tentative values of the heats of formation of cyclo-$C_7H_7^+$ ion and cyclo-$C_7H_7\cdot$ radical are 217 ± 7 and 65 ± 7 kcal./mole, respectively. Estimated bond dissociation energies are $D(C_7H_7\text{–}H)$ in cycloheptatriene = 74 ± 7 kcal./mole and $D(C_7H_7\text{–}C_7H_7)$ in ditropenyl 35 kcal./mole. The cycloheptatrienyl radical was produced by thermal decomposition of ditropenyl and the cyclopentadienyl radical by thermal decomposition of anisole. A number of rearrangement reactions in the thermal decomposition of cyclopentadienyl and cycloheptatrienyl derivatives at low pressures have been observed.

On the basis of molecular orbital theory Hückel[3] predicted that monocyclic conjugated systems having $4n + 2$ π-electrons would have large delocalization energies. Representatives of this group with $n = 1$ are the cyclopentadienyl anion ($C_5H_5^-$), the neutral benzene molecule, and the cycloheptatrienyl (tropenium, tropylium) cation ($C_7H_7^+$). Experimental evidence for the stability of the first two

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[1] National Research Council of Canada Postdoctorate Fellow, 1957–1959.

[2] Work at University of Washington supported in part by the Office of Ordnance Research, U. S. Army.

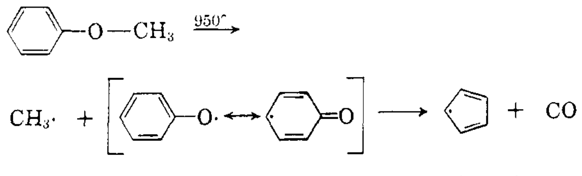
[3] E. Hückel, *Z. Physik*, **70**, 204 (1931); *Z. Elektrochem.*, **43**, 752 (1937).

examples has been known for some time but only relatively recently has the stabilization of the third example been demonstrated, initially by the basic nature of cycloheptatrienone (tropone)[4] and later by the strongly ionic character of tropenium bromide and the stable existence of its perchlorate and fluoroborate salts.[5] Calculations by valence bond or l.c.a.o. molecular orbital methods[3,6,7] indicate that the delocalization energy of the cycloheptatrienyl cation should be much greater than that of its radical and that the delocalization energy of this radical should exceed that of its anion. Similar calculations for the cyclopentadienyl radical and ions[3,6,7] show that although the cyclopentadienyl anion should possess greater delocalization energy than its radical, the corresponding cation should have considerably less. On this basis the ionization potential of the cycloheptatrienyl radical should be lower, due to the removal of an anti-bonding electron, and that of the cyclopentadienyl radical should be higher, due to the removal of a bonding electron, than the ionization potentials of radicals such as allyl and benzyl in which ionization proceeds by removal of a non-bonding electron and for which the simple m.o. theory predicts no difference in delocalization energy between their radicals and ions. It is clear, however, that simple m.o. theory does not describe this situation satisfactorily and that account must be taken of electron interactions to obtain reliable predictions for ions and radicals.[8] Recently, suitably modified m.o. methods have been employed by Combet-Farnoux and Berthier[9] for the estimation of delocalization energies of cyclopentadienyl and cycloheptatrienyl ions and radicals and by Streitwieser[10] for the calculation of the ionization potentials of cyclopentadienyl and cycloheptatrienyl radicals.

No specific detection of these radicals and no measurement of their ionization potentials have been made previously, although estimates of the heats of formation of the related cations have been obtained by electron impact.[11,12] With a view to testing the theoretical predictions of the relative stabilization energies of the cyclopentadienyl and the cycloheptatrienyl cations and radicals, means have been sought to produce these radicals by thermal decomposition reactions and to measure their vertical ionization potentials by electron impact. The energetics of formation of the cycloheptatrienyl cation is also of importance in understanding the dissociative ionization of benzyl derivatives. Meyerson and his co-workers[12] have shown by carbon and deuterium labelling experiments that the $C_7H_7^+$ ion formed from benzyl derivatives at electron energies a few volts greater than $A(C_7H_7^+)$ exhibits a completely symmetrical character with respect to loss of the C_2H_2 fragment and have proposed that the $C_7H_7^+$ ion formed at these energies has the cycloheptatrienyl structure.

Production of the radicals was investigated by the thermal decomposition of suitable derivatives in a fused-silica capillary furnace leading into the ionization chamber of a mass spectrometer.[13] Measurement of the ionization efficiency curves for the radicals and comparison of them with curves for a standard gas were carried out by the method described recently.[14] Since the pressure in the reactor was of the order of 10^{-3} mm., some of the reactions observed in the thermal decompositions studied may have occurred mainly on the surface of the fused-silica capillary.

Cyclopentadienyl Radical.—Pyrolysis of anisole at about 950° was found to proceed to a large extent by the formation of phenoxy and methyl radicals. At slightly higher temperatures the phenoxy radical decomposed to form CO, a free radical of mass 65, and a small amount of a hydrocarbon of mass 66, corresponding to the formula C_5H_6. The ionization potential of the mass 66 hydrocarbon was found to be the same as that of cyclopentadiene measured in a separate experiment (9.00 ± 0.1 v.) and to agree with an earlier value (8.9 v.), also measured by electron impact.[11] A similar production of cyclopentadiene by the pyrolysis of phenol in contact with quartz and glass has been reported.[15] It has also been observed in many cases that introduction of a radical R· into the ionization chamber of a mass spectrometer produces a small yield of the corresponding RH compound, presumably by a surface reaction with some source of abstractable hydrogen.[16] On the grounds that the cyclopentadiene found as a product of the decomposition of anisole was formed in the same way, it was concluded that the radical of mass 65 was the cyclopentadienyl radical, formed most likely by decarbonylation of the intermediate hybrid phenoxy radical.



Cycloheptatrienyl Radical.—Even though tropenium bromide may be sublimed slowly at low pressures and temperatures, it is neither sufficiently volatile nor thermally stable to be considered as a potential source of tropenyl radicals by the

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[4] H. J. Dauben, Jr., and H. J. Ringold, This Journal, **73**, 876 (1951); W. v. E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

[5] (a) W. v. E. Doering and L. H. Knox, *ibid.*, **76**, 876 (1954); (b) H. J. Dauben, Jr., and D. L. Pearson, Abstracts, 126th Meeting, American Chemical Society, New York, N. Y., Sept., 1954; (c) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, This Journal, **79**, 4557 (1957).

[6] J. D. Roberts, A. Streitwieser and C. M. Regan, *ibid.*, **74**, 4579 (1952).

[7] J. L. Franklin and F. H. Field, *ibid.*, **75**, 2819 (1953).

[8] A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954); N. S. Hush and J. A. Pople, *ibid.*, **51**, 600 (1955); G. Berthier, *J. chim. phys.*, **52**, 141 (1955); H. C. Lefkovits, J. Fain and F. A. Matsen, *J. Chem. Phys.*, **23**, 1690 (1955); H. D. Hunt, D. L. Peterson and W. T. Simpson, *ibid.*, **27**, 20 (1957).

[9] F. Combet-Farnoux and G. Berthier, *Compt. rend.*, **248**, 688 (1959), and private communication.

[10] A. Streitwieser, Jr., This Journal, **82**, 4123 (1960).

[11] J. Hissel, *Bull. soc. roy. sci. Liège*, **21**, 457 (1952).

[12] (a) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957); (b) P. N. Rylander, S. Meyerson and H. M. Grubb, This Journal, **79**, 842 (1957); (c) S. Meyerson, P. N. Rylander, E. E. Eliel and J. D. McCollum, *ibid.*, **81**, 2606 (1959).

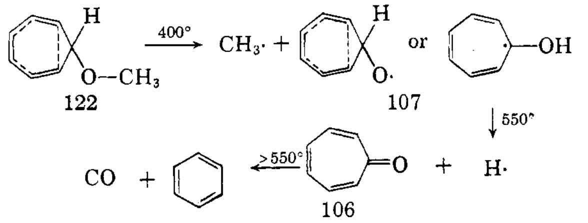
[13] J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

[14] F. P. Lossing and J. B. de Sousa, This Journal, **81**, 281 (1959).

[15] H. E. Roscoe, *Ann.*, **232**, 348 (1886); S. Ruhemann, *Erdöl u. Teer*, **5**, 455 (1929); P. J. Wilson, Jr., and J. H. Wells, *Chem. Revs.*, **34**, 1 (1944).

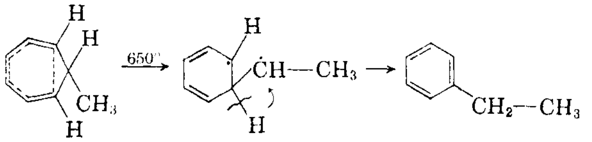
[16] F. P. Lossing, *Can. J. Chem.*, **35**, 305 (1957).

present technique. The related covalent tropenyl methyl ether possesses the necessary volatility but was found to undergo thermal decomposition by a path analogous to that shown by anisole



At a furnace temperature of 400° a radical of mass 107 was formed and easily detected using electrons of low energy. At 550° this radical was largely decomposed, and a substance of mass 106 was produced which had a mass spectrum that showed definitely that it was not benzaldehyde. At temperatures above 550° this species was unstable, and benzene and CO were formed in large amounts. The identity of the mass 106 species is not known but in view of its non-identity with benzaldehyde and its decarbonylation to give benzene at higher temperatures, tentatively it may be assumed to be tropone. It follows then that the mass 107 fragment may be either tropenyloxy radical or hydroxytropenyl radical; the relatively low temperature needed for its formation implies resonance stabilization and consequently favors the latter formulation. No tropenyl radicals could be detected as decomposition products from tropenyl methyl ether but methyl radicals were detected in abundance.

Pyrolysis of 7-methylcycloheptatriene, synthesized by a convenient new method (see Preparation of Materials, below), offered another possible source of tropenyl radicals. Instead of losing methyl radical, however, this compound was found to rearrange at 650° to ethylbenzene, probably by the reaction course

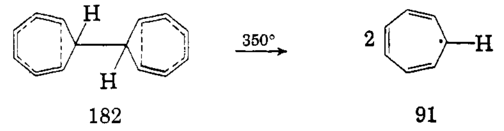


The heat of formation of 7-methylcycloheptatriene can be calculated from ΔH_f(cycloheptatriene) = 43.47 kcal./mole[17] using Franklin's group equivalent method[18]

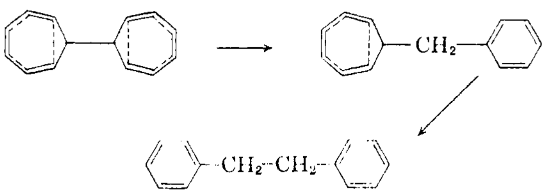
$$\begin{aligned}\Delta H_f(\mathrm{C_7H_7CH_3}, \text{gas}, 25°) &= \Delta H_f(\mathrm{C_7H_7{-}H}) - \Delta H_f(\mathrm{-CH_2-}) + \Delta H_f(\mathrm{>CHCH_3}) \\ &= 43.47 - (-4.93) + (-11.21) \\ &= 37.19 \text{ kcal./mole}\end{aligned}$$

Since ΔH_f(ethylbenzene) = 7.12 kcal/mole,[19] the observed isomerization is exothermic by 30 kcal./mole and probably is facilitated also by significant transannular bonding between the ends of the conjugated system.

Tropenyl radicals were obtained in satisfactory yield by the pyrolysis of bitropenyl (bis(7-cycloheptatrienyl), dihydroheptafulvalene). The temperature at which the decomposition was almost



complete, 350°, was remarkably low, being about the same as that at which alkyl nitrites were partially decomposed under the same conditions,[14] and about 400° lower than the temperature required to decompose bibenzyl. Assuming no special catalytic effects, this suggests that the dissociation energy for the central C–C bond in bitropenyl is roughly the same or slightly lower than for the RO–NO bond in alkyl nitrites (37 kcal./mole)[20] and considerably weaker than the central C–C bond in bibenzyl (*ca.* 47 kcal./mole[21]). In addition to the cycloheptatrienyl radical, a substance of mass 182 was formed in the pyrolysis of bitropenyl. Although the mass 181 peak of bitropenyl decreased with decomposition above 320°, the mass 182 peak increased. Evidently some species having a 182/181 peak ratio greater than that of the parent compound was being formed. Comparison of the peak ratios for bitropenyl and bibenzyl as measured in this spectrometer, summarized in Table I, indicates that bibenzyl gives a relatively larger parent peak than bitropenyl and suggests that the mass 182 product formed from pyrolysis of bitropenyl is bibenzyl. It seems clear that the bibenzyl was not formed by recombination of tropenyl radicals which had isomerized to benzyl radicals, since no sign of a break in the ionization efficiency curve for the tropenyl radical was observed at the ionization potential of benzyl radical. It is probable, therefore, that the bibenzyl was formed by an isomerization of bitropenyl similar to that observed for 7-methylcycloheptatriene



The heat of formation of bitropenyl can be calculated from that for cycloheptatriene[17] using Franklin's group equivalent method[18]

$$\begin{aligned}\Delta H_f(\mathrm{C_7H_7{-}C_7H_7}, \text{gas}, 25°) &= 2[\Delta H_f(\mathrm{C_7H_7{-}H}) - \Delta H_f(\mathrm{-CH_2-}) + \Delta H_f(\mathrm{>CH-})] \\ &= 2[43.47 - (-4.93) + (-1.09)] \\ &\ 94.62 \text{ kcal./mole}\end{aligned}$$

Inasmuch as ΔH_f(bibenzyl) = 27.8 kcal./mole[22] the isomerization of bitropenyl to bibenzyl is exothermic by about 67 kcal./mole and its occurrence at 350° is not surprising. 7-Benzylcycloheptatriene may be an intermediate in this isomerization but

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[17] H. L. Finke, D. W. Scott, M. E. Gross, J. E. Messerly and G. Waddington, THIS JOURNAL, **78**, 5469 (1956).

[18] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

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

[20] P. Gray and A. Williams, *Chem. Revs.*, **59**, 240 (1959).

[21] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958.

[22] S. W. Benson and J. H. Buss, *J. Phys. Chem.*, **61**, 104 (1957).

its detection in this system would be extremely difficult.

Results and Discussion

The measured ionization potentials of cyclopentadienyl and cycloheptatrienyl radicals are given in Table II, together with the change in delocalization energy between radicals and carbonium ions calculated by the simple m.o. theory[6,7] and the ionization potentials recently calculated by Streitwieser using a modified m.o. method.[10] The observed ionization potentials are qualitatively in accord with the predictions by the simple m.o. method. The high ionization potential of cyclopentadienyl radical, higher than that found for any other hydrocarbon radical except methyl and ethyl radicals, reflects the decrease in stabilization expected on going from the radical to the cyclopentadienyl cation. The extremely low ionization potential of cycloheptatrienyl radical, lower than that reported for any other hydrocarbon radical, shows that the cycloheptatrienyl cation has considerably greater delocalization energy than its radical. This is in agreement with other evidence for the great stability of the cycloheptatrienyl cation.[4,5] The ionization potentials of radicals such as allyl (8.16 v.)[23] and benzyl (7.76 v.)[24] for which the simple m.o. theory predicts (incorrectly) no change in delocalization energy in going to the ions lie between these two extremes. The agreement between the experimental ionization potentials and those calculated by Streitwieser using his modified m.o. method (coulomb integral variation) is excellent.

TABLE I

PARTIAL MASS SPECTRA

Mass no.	Bitropenyl	Bibenzyl
182	0.62	20.3
181	2.17	0.14
91	100.0	100.0

TABLE II

IONIZATION POTENTIALS OF RADICALS

Radical	Ionization potential (v.)	Calcd.[3,6,7] ΔD.E. for $CnHn\cdot \rightarrow CnHn^+$ (β units)	Calcd.[10] ioniz. poten.
Cyclo-$C_5H_5\cdot$	8.69 ± 0.1	−0.62	8.82
Cyclo-$C_7H_7\cdot$	6.60 ± 0.1	+0.45	6.41

NOTE ADDED IN PROOF.—The ionization potential of cyclopentadienyl radical has been re-determined using radicals formed by the thermal decomposition of di-cyclopentadienyl nickel, which was supplied through the courtesy of Dr. W. B. Ligett of the Ethyl Corporation Research Laboratories. At 950–1000 a good yield of cyclopentadienyl radicals was obtained from this compound. The average of a number of measurements of the ionization potential of the radical was 8.76 ± 0.1 v., in satisfactory agreement with the value of 8.69 ± 0.1 v. given above.

The appearance potential data for the cyclo-$C_5H_5^+$ and cyclo-$C_7H_7^+$ ions are rather ambiguous. The appearance potential found in the present work for the $C_5H_5^+$ ion from cyclopentadiene (Table III) is considerably higher than an earlier value of 10.7 v.[11] Samples of cyclopentadiene (Abco Chemical Co., Jasonols Chemical Corp.) were all found to produce a number of peaks above mass 66, even after several purifications by gas chromatography immediately followed by refrigeration. This treatment should have removed any dimer present. In view of the high proton affinity of cyclopentadiene in the gas phase,[25] condensation of fragment carbonium ions with cyclopentadiene may have produced the higher mass ions, although such reactions usually are observed only at higher pressures than used in the present work. Whether for these reasons or not the ionization efficiency curves for $C_5H_5^+$ ions from these samples had long "tails" and estimation of the appearance potential was quite uncertain. It is evident, by comparison with I(cyclo-$C_5H_5\cdot$), that the observed appearance potential is much too high to correspond to the formation of cyclopentadienyl cation with no excess energy. The present data consequently cannot be used to calculate ΔH_f(cyclo-$C_5H_5^+$) or D(cyclo-C_5H_5–H).

The appearance potentials for $C_7H_7^+$ ion formation from cycloheptatriene and from 7-methylcycloheptatriene are given in Table III. Owing to an appreciable amount of "tailing" at the foot of the ionization efficiency curves, it is probable that the $C_7H_7^+$ ion is being formed with excess energy and that heats of formation and bond dissociation energies derived from these appearance potentials should be regarded as upper limits. When combined with the heats of formation of cycloheptatriene and 7-methylcycloheptatriene, the two appearance potentials lead to an upper limit of 224 kcal./mole for ΔH_f(cyclo $C_7H_7^+$). From I(cyclo-$C_7H_7\cdot$) = 6.60 v. and ΔH_f(bitropenyl) = 94.6 kcal./mole (see above), this value leads to $D(C_7H_7–C_7H_7)$ = 49 kcal./mole. This result is definitely too high to be compatible with the evidence from the thermal decomposition for a value somewhat less than 37 kcal./mole for the dissociation energy of this bond. Although the evidence from the thermal decomposition is rather approximate, it appears that this bond must be considerably weaker than the central bond in bibenzyl (47 kcal./mole[21]), as discussed above. Possibly the best compromise estimate that can be made from the pyrolytic and electron impact evidence is that $D(C_7H_7–C_7H_7)$ is about 35 kcal./mole and that ΔH_f(cyclo-$C_7H_7^+$) is consequently about 217 kcal./mole. Other thermochemical values based on this estimate are given in Table IV. The vertical resonance energies of the radical and the ion[26] were calculated using the relations

$$
\begin{aligned}
RE_{\text{vert}}(\text{cyclo-}C_7H_7\cdot) &= D(CH_3–H) - D(C_7H_7–H) \\
RE_{\text{vert}}(\text{cyclo-}C_7H_7^+) &= A(CH_3^+)_{CH_4} = A(C_7H_7^+)_{C_7H_8} \\
&= [\Delta H_f(CH_3^+) - \Delta H_f(CH_4)] - \\
&\qquad [\Delta H_f(C_7H_7^+) - \Delta H_f(C_7H_8)]
\end{aligned}
$$

The values in Table IV probably are uncertain to ±7 kcal./mole. with a larger uncertainty for $D(C_7H_7–C_7H_7)$.

It is interesting to compare the heat of formation obtained above for cyclo-$C_7H_7^+$ with the heat of formation of the benzyl ion, $C_6H_5CH_2^+$. The

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[23] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

[24] J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, *ibid.*, **22**, 1948 (1954).

[25] F. W. Lampe and F. H. Field, *Tetrahedron*, **7**, 189 (1959).

[26] Comparison of these experimental values for the vertical resonance energies and of the derived empirical resonance energies with values calculated by modified m.o. methods will be considered in a subsequent paper.

TABLE III

IONIZATION AND APPEARANCE POTENTIALS IN CYCLOPENTADIENYL AND CYCLOHEPTATRIENYL DERIVATIVES

Transition	Energy (volts) This work	Energy (volts) Literature	ΔH_f, ion (kcal./mole)
Cyclo-$C_5H_6 \rightarrow C_5H_5^+ + H\cdot$	(<12.6)	10.7[11]	....
Cyclo-$C_7H_8 \rightarrow C_7H_7^+ + H\cdot$	$\leqslant 10.1 \pm 0.2$	10.4[12a]	$C_7H_7^+ \leqslant 224$
7-Me-$C_7H_7 \rightarrow C_7H_7^+ + CH_3\cdot$	$\leqslant 9.5 \pm .2$	....	$C_7H_7^+ \leqslant 224$
Cyclo-$C_5H_6 \rightarrow C_5H_6^+$	$9.00 \pm .1$	8.9[11]; 8.91 (calcd.)[10]	$C_5H_6^+ \leqslant 239$
Cyclo-$C_7H_8 \rightarrow C_7H_8^+$	$8.55 \pm .1$	7.89 (calcd.)[10]	$C_7H_8^+ \leqslant 241$

TABLE IV

ESTIMATED THERMOCHEMICAL PROPERTIES OF CYCLOHEPTATRIENYL CATION AND RADICAL IN KCAL./MOLE

ΔH_f-($C_7H_7^+$)	ΔH_f-($C_7H_7\cdot$)	D-(C_7H_7–H)	D(C_7H_7–C_7H_7)	vert. RE-($C_7H_7^+$)	vert. RE ($C_7H_7\cdot$)
217	65	74	35	106	28

latter can be calculated from the heat of formation and the ionization potential of benzyl radical. Although there are some discrepancies in the thermochemical and kinetic data for $\Delta H_f(C_6H_5CH_2\cdot)$, it seems quite certain that the value lies in the range of 38–44 kcal./mole.[22,27] Taken with $I(C_6H_5CH_2\cdot) = 7.76$ v.,[24] this leads to $\Delta H_f(C_6H_5CH_2^+) = 217$–$223$ kcal./mole. This is essentially the same as the value of ΔH_f(cyclo-$C_7H_7^+$) estimated from the present work. The near equivalence of these ionic heats of formation may raise some question as to whether the two ionic species are not in fact the same ion. It seems clear, however, from the derivation of these values that the heats of formation do refer to two different ionic species. The value of $\Delta H_f(C_6H_5CH_2^+)$ is based on measurements of the heat of formation and of the electron impact ionization potential performed on radicals which are unequivocally benzyl radicals. Since ionization by electron impact is a vertical process in the Franck–Condon sense, the ionization threshold for benzyl radical must correspond to the energy required to form benzyl ion, although one that is quite possibly not in its lowest vibrational state. A subsequent isomerization of benzyl ion to a symmetrical $C_7H_7^+$ ion, such as appears to occur in dissociative ionization processes at higher electron energies,[12] would not alter the assignment of this threshold energy to the process $C_6H_5CH_2\cdot \rightarrow C_6H_5CH_2^+$. The derivation of ΔH_f(cyclo-$C_7H_7^+$) is based similarly on ΔH_f(cyclo-$C_7H_7\cdot$) and I(cyclo-$C_7H_7\cdot$). The value of the former is based in part on an estimate of $D(C_7H_7$–$C_7H_7)$ from the thermal decomposition of bitropenyl. Even though the isomerization of cyclo-$C_7H_7\cdot \rightarrow C_6H_5CH_2\cdot$ would be exothermic by some 20 kcal./mole, the observed large difference in ionization potential clearly shows that the radicals produced by thermal decomposition of bitropenyl are cycloheptatrienyl radicals and have not isomerized to benzyl radicals. It may be concluded, therefore, that the heats of formation of cycloheptatrienyl and benzyl cations are not greatly different, although the latter may be greater by about 7 kcal./mole.

A value for ΔH_f(cyclo-$C_7H_7^+$) of 209 kcal./mole, somewhat lower than that given above, has been proposed recently. From tracer studies Meyerson and co-workers have found that $C_7H_7^+$ ions formed from dissociative ionization of benzyl hydrocarbons[12a,b] and of benzyl chloride and alcohol[12c] appear to have a symmetrical structure, and they have proposed that these are not benzyl, but instead cycloheptatrienyl, cations. Although from the nature of the experiments it could not be demonstrated that $C_7H_7^+$ ions formed at or just above the energy threshold for their production had the same characteristics, nevertheless their proposal throws considerable doubt on the energies of benzyl ion formation derived from dissociative ionization processes. They also pointed out[12c] that $\Delta H_f(C_7H_7^+)$ derived from appearance potentials of $C_7H_7^+$ ions from benzyl halides, together with heats of formation of the halides calculated from published bond dissociation energies, appears to be 6–10 kcal./mole lower than that obtained from $\Delta H_f(C_6H_5CH_2\cdot) + I(C_6H_5CH_2\cdot)$. This discrepancy is independent of the value chosen for $\Delta H_f(C_6H_5CH_2\cdot)$. It should be noted, however, that the value of 209 kcal./mole which they derive for $\Delta H_f(C_7H_7^+)$ should not be regarded as a maximum, as they claim, since it is calculated using $\Delta H_f(C_6H_5CH_2\cdot) = 37.5$ kcal./mole, which is itself not consistent with the bond dissociation data and the preferred values for the heats of formation of benzyl halides.[28] Using $\Delta H_f(C_6H_5CH_2\cdot) = 43$ kcal./mole, as recommended by Benson and Buss[22] and Sehon and Szwarc,[27] the estimate of Meyerson, *et al.*, for $\Delta H_f(C_7H_7^+)$ would be increased to about 215 kcal./mole, in reasonably good agreement with the value for ΔH_f(cyclo-$C_7H_7^+$) proposed in this work. On the same basis $\Delta H_f(C_6H_5CH_2^+)$ derived from $\Delta H_f(C_6H_5CH_2\cdot) + I(C_6H_5CH_2\cdot)$ would be 222 kcal./mole, or about 5 kcal./mole greater than the preferred value for ΔH_f(cyclo-$C_7H_7^+$) derived similarly in the present work. In view of uncertainties in the appearance potentials, and in the thermochemical and kinetic data, it is doubtful whether this apparent difference in the heats of formation of benzyl ion and cycloheptatrienyl ion is large enough to enable decision to be made on this ground as to the identity of the $C_7H_7^+$ ions formed from benzyl derivatives. It should be noted further that if ΔH_f(cyclo-$C_7H_7^+$) were as low as 209 kcal./mole, then from I(cyclo-$C_7H_7\cdot$) as measured in this work, $D(C_7H_7$–$C_7H_7)$ would be only 19 kcal./mole. This is much too low to be compatible with the observed thermal stability of bitropenyl. The authors feel, therefore, that the values given in Table IV are to be preferred.

The ionization potentials measured for cyclopentadiene and cycloheptatriene and the corresponding ionic heats of formation of the molecular

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(27) A. H. Sehon and M. Szwarc, *Ann. Rev. Phys. Chem.*, **8**, 439 (1957).

(28) The data used by these workers imply heats of formation for the benzyl halides (Cl, −1.5; Br, +13.7; I, +29.8 kcal./mole) that are 6–9 kcal./mole lower than the best available thermochemical values (F. W. Kirkbride, *J. Appl. Chem. (London)*, **6**, 11 (1956); ref. 22).

ions (using $\Delta H_f(\text{cyclo-C}_5\text{H}_6) = 31.84$ kcal./mole[29] and $\Delta H_f(\text{cyclo-C}_7\text{H}_8) = 43.47$ kcal./mole[17]), are included in Table III. The agreement of $I(\text{cyclo-C}_5\text{H}_6)$ with the value of Hissell[11] and the calculated value of Streitwieser[10] is satisfactory. For cycloheptatriene the observed ionization potential is appreciably higher than the calculated value. This disagreement probably arises from the fact that the latter was calculated on the assumption that there was no transannular interaction between the ends of the conjugated system. The thermal reactions of cycloheptatrienyl derivatives observed in this work, as well as other evidence, support the view that such interaction is quite strongly developed.

Preparation of Materials

Cycloheptatriene.—Bicyclo[2.2.1]heptadiene (from Shell Chemical Co.) was thermally isomerized to cycloheptatriene essentially as described by the supplier. Purification was effected by double distillation through a small (5 × 440 mm.) Nester spinning-brush fractionation column at atmospheric pressure. The sample used in the present study was shown to be at least 99.2% cycloheptatriene by vapor phase chromatography (Aerograph silicone column).

7-Methoxycycloheptatriene (Tropenyl Methyl Ether).—Use of the more readily available and tractable tropenium (cycloheptatrienylium) fluoroborate[5c] or perchlorate[5c] salts instead of tropenium bromide necessitated certain modifications in the method originally employed by Doering and Knox.[5a] Finely divided tropenium fluoroborate (44.2 g., 0.25 mole) was added to a solution of commercial sodium methoxide (15.2 g., 0.30 mole) in absolute methanol (300 ml.) and the mixture swirled until all of the salt had dissolved (*ca.* 30 min.; a trace of fine solid separates). The solution was diluted with pentane (300 ml.), extracted with water (4 × 200 ml.) and each aqueous extract back-extracted cascade-fashion with the same portions of pentane (4 × 200 ml.). The combined organic layers were dried (magnesium sulfate) and concentrated on a rotary evaporator without external warming. Distillation of the residual light yellow oil in a Claisen–Vigreux apparatus gave colorless 7-methoxycycloheptatriene (24.5 g., 81% yield; b.p. 54–55°(13 mm.); n^{25}_{D} 1.5092; $\lambda_{\max}$ (pentane), 256 mμ (3480)). 7-Methoxycycloheptatriene has a rather penetrating, characteristic odor and exposure to low vapor concentrations may induce headaches. Similar yields (70–80%) may be realized by the use of tropenium perchlorate and only minor modifications. Due to its extreme shock sensitivity, *no attempt should be made to pulverize tropenium perchlorate* in order to accelerate the heterogeneous reaction.

7-Methylcycloheptatriene.—While the preparation of 7-methylcycloheptatriene by the interaction of a methyl Grignard reagent and tropenium bromide was first mentioned by Doering and Krauch,[30] details of its preparation by this method and its physical constants were reported first by Abel, Bennett, Burton and Wilkinson.[31] To circumvent the difficulties arising from the very low solubility of tropenium bromide in ether, tropenyl methyl ether has been employed as an ether-soluble source of tropenium ions for reaction with methylmagnesium bromide and synthesis of 7-methylcycloheptatriene. Insofar as we know, this represents the first demonstration that an ionogenic ether will undergo a condensation reaction with a Grignard reagent, although the ability of magnesium halides or Grignard reagents to effect cleavage of certain ethers at elevated temperatures is well-known.

A solution of 7-methoxycycloheptatriene (6.92 g., 0.057 mole) in dry ether (10 ml.) was added dropwise to a mechanically stirred solution of methylmagnesium bromide in dry ether (1.6 g. magnesium, 0.067 mole; 6.8 g. methyl bromide, 0.072 mole; 100 ml. ether); a white precipitate formed as each drop contacted the solution but rapidly dissolved. After stirring at room temperature for about 6 hr., dilute hydrochloric acid (*ca.* 25 ml.) was added and the ether layer separated. Rotary evaporation of the ether without external heating followed by dissolution in pentane and similar evaporation left a liquid residue which was distilled through a small Claisen distillation apparatus and separated arbitrarily into five fractions ($n^{26.2}_{\mathrm{D}}$ 1.5032–1.5055; total yield, 3.32 g.). Assay of portions of the combined center fractions by hydride exchange with trityl perchlorate in methylene chloride gave 86.5% methyltropenium perchlorate[5c] and 84.5% triphenylmethane and by gas chromatographic analysis (Aerograph silicone column) indicated 94.5% 7-methylcycloheptatriene content. Accordingly, 7-methylcycloheptatriene was obtained in 40–45% yield and the combined center fractions, which were used in the present study, had the physical constants: b.p. 138–139° (corr.)/atm. press. (capillary tube method); $n^{24.5}_{\mathrm{D}}$ 1.5028; $\lambda_{\max}$(pentane), 257 mμ; (reported[31]: b.p. 50° (35 mm.), n^{20}_{D} 1.5050). Since the distillation residue contained considerable unreacted tropenyl methyl ether, the yield of 7-methylcycloheptatriene probably could be increased by conduct of the reaction at the reflux temperature of ether or tetrahydrofuran.

Bis-(7-cycloheptatrienyl) (Bitropenyl, *Dihydroheptafulvalene*).—Substitution of tropenium fluoroborate or perchlorate for the bromide salt and conduct of the reaction on a large scale required certain modifications in the procedure used by Doering and Knox.[5a] Tropenium fluoroborate (24.5 g., 0.138 mole) was dissolved in water (300 ml.), zinc dust (Mallinckrodt Analytical Reagent Grade, 9.9 g., 0.152 mole) added and the reaction mixture shaken vigorously in a separatory funnel or stirred mechanically (*ca.* 60 min.). The pentane extracts (4 × 100 ml.) of the reaction mixture were combined, washed with water, dried and concentrated on a rotary evaporator to give crude bis-(7-cycloheptatrienyl) as a pale yellow crystalline residue (11.0 g., 87.8% yield). Sublimation at 50° (0.1 mm.) gave complete recovery but failed to remove the yellow impurity. Chromatography on alumina (Merck "basic," 15:1) using pentane as eluting solvent gave a product (10.2 g.) containing only a trace of yellow impurity which was removed by repetition of the chromatography (white crystals, m.p. 61°, 77.4% yield, $\lambda_{\max}$(pentane) 252 mμ (6740); reported,[5a] m.p. 61°). Tropenium perchlorate may be employed in a similar procedure but longer reaction times (2 days) are needed and the yields are less consistent (50–90% crude), possibly due to coating of the surface of the zinc dust. Warming of the aqueous solution of tropenium perchlorate to accelerate the reaction leads to the formation of dark-brown by-products.

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[29] Calculated from the heat of hydrogenation value at 82° (G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, This Journal, **58**, 146 (1936)) after correction to 25° by $\Delta C_{\mathrm{PH}} = -0.005$ kcal./degree/double bond.

[30] W. v. E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956).

[31] E. W. Abel, M. A. Bennett, R. Burton and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).