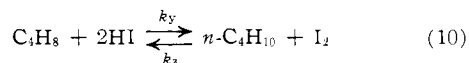


four-center reactions recently proposed by Benson and Bose.²³

At the lower temperatures the measured amount of butadiene corresponds closely to the value given by the equilibrium constant ($K_A = k_v/k_x$) calculated from API²⁴ and JANAF⁵ data. At 572°K. significantly less butadiene than expected was found, presumably due to radical-catalyzed polymerization reactions.²⁵

The formation of HI from (8) starts the very slow reaction y.



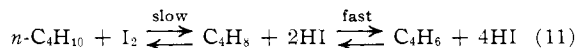
(23) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963).

(24) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

(25) G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 725 (1939).

The equilibrium for the formation of *n*-butane is established very slowly, and as shown in Table II only insignificant traces of *n*-butane are formed.

The speed of formation of butadiene is so great compared to the slow reaction z that it leads to the interesting prediction that starting with *n*-butane and iodine the initial product should be butadiene and HI rather than the butenes. The entire scheme would be



The result would be an early establishment of the $\text{C}_4\text{H}_6 + 4\text{HI}$ equilibrium followed by a slow return to the butene equilibrium at which point there would be negligible C_4H_6 . Two rough experiments were made with $\text{C}_4\text{H}_{10} + \text{I}_2$ at about 300°C. and found roughly to verify this type of equilibrium "overshoot."

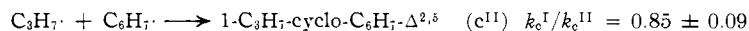
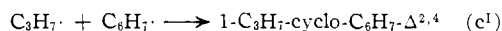
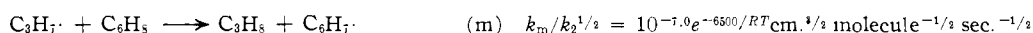
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, BRITISH COLUMBIA, CANADA]

A Kinetic Study of the Cyclohexadienyl Radical. I. Disproportionation and Combination with the Isopropyl Radical

BY D. G. L. JAMES AND R. D. SUART

RECEIVED JULY 27, 1964

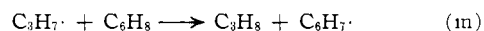
The kinetics of the generation and reactions of the cyclohexadienyl radical with the isopropyl radical may be described by the equations



The mechanism of combination and disproportionation is discussed in relation to these results. A loosely bonded transition state is suggested; the course of reaction appears to be sensitive to the distribution of free valence in the reactants and rather insensitive to delocalization energy in the products.

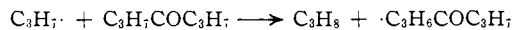
Among the alkyl radicals, the ratio of disproportionation to combination normally increases with an increasing degree of substitution at the reactive carbon atom. This trend is illustrated by the values¹ of k_d/k_c for the series $[\text{CH}_3\text{CH}_2\cdot, 0.14] < [(\text{CH}_3)_2\text{CH}\cdot, 0.65] < [(\text{CH}_3)_3\text{C}\cdot, 4.2]$. Moreover, the value of 0.5 for cyclohexyl places this radical in the same class as the structurally related isopropyl radical. On that basis alone, we might predict that the cyclohexadienyl radical should also belong to this class; however, the formation of the highly stabilized molecule benzene in the disproportionation step may well favor disproportionation abnormally over combination. To estimate the relative importance of the structural and energetic factors we have studied the system [cyclohexadienyl + isopropyl].

A convenient system for the study of the interaction of isopropyl and cyclohexadienyl radicals is provided by the photolysis of the mixed vapors of diisopropyl ketone and cyclohexadiene-1,4 in the range 75 to 136°. The isopropyl radical is formed directly by photolysis of the ketone, and the cyclohexadienyl radical by subsequent metathesis



To simplify the kinetics of the system the mutual interaction of cyclohexadienyl radicals was suppressed by maintaining the isopropyl radical in large excess over the cyclohexadienyl radical; this is easily arranged under the stated conditions.

A preliminary study of the photolysis of pure diisopropyl ketone was undertaken to establish the mechanism over the range 71 to 193° and to measure the rate of the metathetical reaction



The latter was a prerequisite for the measurement of the rate of reaction m, which generates the cyclohexadienyl radical. Previous investigations^{2,3} of this reaction have covered the range 100 to 400°, and, in view of the complexities at higher temperatures, it is desirable to confirm that the extrapolation to this low range is sufficiently precise.

Experimental

The apparatus and method have been described in two earlier papers.^{4,5} Certain improvements in the techniques of purification

(1) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Chem. Kinet.*, **1**, 105 (1961).

(2) C. A. Heller and A. S. Gordon, *J. Phys. Chem.*, **60**, 1315 (1956).

(3) C. A. Heller and A. S. Gordon, *ibid.*, **62**, 709 (1958).

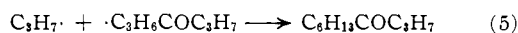
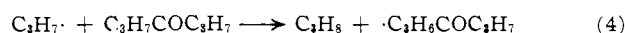
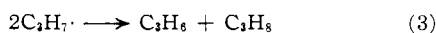
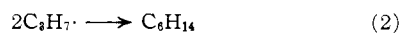
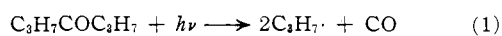
of the reactants and analysis of the products have been adopted in this investigation. The materials, diisopropyl ketone from the K and K Laboratories and cyclohexadiene-1,4 from the Aldrich Chemical Co., were purified by gas chromatography, using the 12-ft. Apiezon J column of the Beckman Megachrom instrument at 95 and 75°, respectively. The resultant diisopropyl ketone was essentially pure, but the cyclohexadiene-1,4 still contained rather less than 0.1% of benzene; this was estimated and a correction applied to the results wherever appropriate.

The analysis followed the pattern of fractionation into CO, C₃, C₆, and residual samples, supplemented by analysis by gas chromatography. The CO fraction was separated at -210°, measured on the gas buret, and found to be pure and free from traces of methane. The C₃ fraction was separated at -140°, measured, transferred, passed in a stream of nitrogen through a 2-m. silica gel column at 110°, and analyzed by a flame-ionization detector; it consisted entirely of C₃H₆ and C₃H₈. The C₃H₆/C₃H₈ ratio could then be measured by a comparison of peak areas if the area of the C₃H₈ peak was multiplied by 0.913. For systems containing no cyclohexadiene-1,4 the C₆ fraction was separated at -94°, found to be pure diisopropyl, and estimated by the gas buret using a suitable correction for nonideal behavior. When cyclohexadiene-1,4 was present, the C₆ fraction was combined with the residue, a known amount of *n*-heptane was added to serve as an internal standard, and the whole mixture was isolated under vacuum in a sealed tube. Immediately before analysis the tube was cooled in liquid air, opened, and 20 μl. of *n*-pentane was added as a diluent. Two distinct chromatographic analyses were performed: (a) for diisopropyl and benzene, and (b) for C₆H₁₄ isomers. Analysis a was performed with a 2-m. packed polyethylene glycol column at 52°, using the flame-ionization detector of the Perkin-Elmer Model 154C chromatograph. Peak areas were measured for C₆H₁₄, C₆H₆, C₇H₁₆, and C₆H₈; the last was necessary as the cyclohexadiene-1,4 contained a measurable trace of benzene, and the small correction could then be made. The molar ratio C₆H₁₄/C₇H₁₆ was obtained from the peak areas if the area of the C₆H₁₄ peak was multiplied by 1.165, and the molar ratio C₆H₆/C₇H₁₆ was obtained if the corrected area of the C₆H₆ peak was multiplied by 1.095. Analysis (b) was performed with the Perkin-Elmer Model 226 chromatograph, using the 150-ft. polyethylene glycol capillary column, first at room temperature for 10 min., and subsequently at 120°. This allowed the initial passage and identification of peaks corresponding in order to C₆H₁₄, C₇H₁₆, C₆H₈, C₆H₆, and (C₃H₇)₂CO, and two final peaks considered to be the C₆H₁₄ isomers 1-isopropylcyclohexadiene-2,4 (I) and 1-isopropylcyclohexadiene-2,5 (II). The identification of the earlier peak with I and the later peak with II is described in the Discussion section.

The preliminary photolytic study of pure gaseous diisopropyl ketone covered the range 71 to 193°. Particular care was taken to look for the isobutyraldehyde and dimethylketene reported tentatively for photolyses at room temperature.³ No isobutyraldehyde was detected using the 150-ft. polyethylene glycol capillary column with the Perkin-Elmer Model 226 chromatograph, although it had been established that trace amounts of isobutyraldehyde would be detected by this method, and no peak for dimethylketene was observed. The kinetic evidence also excludes the formation of isobutyraldehyde and dimethylketene in significant amounts.

Results and Discussion

The Photolysis of Pure Diisopropyl Ketone.—Twelve experiments were performed on the photolysis of pure diisopropyl ketone vapor over the range 71 to 193°. The results are consistent with the simple mechanism



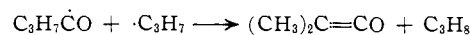
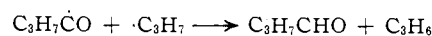
(4) D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A244**, 289 (1958).

(5) D. G. L. James and E. W. R. Steacie, *ibid.*, **A244**, 297 (1958).

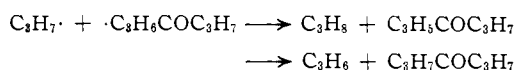
This mechanism requires that one molecule of carbon monoxide should be equivalent to two isopropyl radicals, and hence to one molecule of either propane or diisopropyl. The observed value of the ratio

$$M = \frac{R(\text{C}_3\text{H}_8) + R(\text{C}_6\text{H}_{14})}{R(\text{CO})} = 0.99 \pm 0.05$$

therefore confirms this simple mechanism, and the observed ratio $k_3/k_2 = 0.58 \pm 0.04$ is also in good agreement with the previous value.² In particular, these ratios allow us to dismiss as negligible both participation of the isobutyryl radical in the reaction scheme and disproportionation of the reactants of reaction 5. If the isobutyryl radical were present, both isobutyraldehyde and dimethylketene would be expected^{2,3}



Neither compound could be found among the products, although the sensitive methods of detection described above were used. Furthermore, both reactions would increase M and the former would increase k_3/k_2 , whereas each quantity is slightly below the accepted value.^{1,2} The reactions of disproportionation which might compete with reaction 5 are



The former reaction would increase M and the latter k_3/k_2 , and each increase would be larger the higher the temperature. Neither quantity is high or dependent upon temperature. The former reaction also forms isopropenyl isopropyl ketone, but no peak for this substance was found on the chromatograms. Accordingly reactions 1-5 represent adequately the mechanism of the photolysis of the pure ketone between 71 and 193°.

Values of $k_4/k_2^{1/2}$ were obtained from the equation

$$k_4/k_2^{1/2} = \{R(\text{C}_3\text{H}_8) - R(\text{C}_3\text{H}_6)\}/[\text{D}]R(\text{C}_6\text{H}_{14})^{1/2} \quad (6)$$

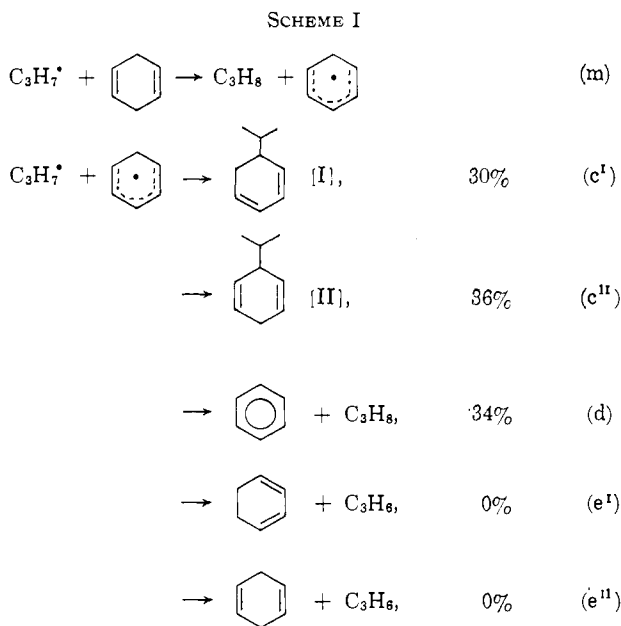
where [D] is the concentration of the ketone and $R(\text{X})$ is the rate of formation of product X; they were in good agreement with the results of Heller and Gordon.² We have, therefore, confirmed the simplicity of the mechanism in the low temperature range and established diisopropyl ketone as a suitable source of the isopropyl radical for this investigation.

The Generation and Reactions of the Cyclohexadienyl Radical.—Fourteen experiments were performed on the photolysis of the gaseous mixture of diisopropyl ketone and cyclohexadiene-1,4 between 75 and 136°. The results are listed in Table I, where [D] and [B] signify the concentration of the ketone and the cyclohexadiene-1,4, respectively, in molecules/cm.³, and $R(\text{X})$ represents the rate of formation of the product X in molecules/cm.³ sec. The ratio $k_3/k_2 = R(\text{C}_3\text{H}_8)/R(\text{C}_6\text{H}_{14})$ has here the value of 0.60 ± 0.05 , in harmony with the value of 0.58 ± 0.04 obtained in the photolysis of the pure ketone. This agreement confirms that the only significant source of propene is the disproportionation of isopropyl radicals. The ratio $M = \{R(\text{C}_3\text{H}_8) + R(\text{C}_6\text{H}_{14})\}/R(\text{CO})$ consistently exceeds unity, indicating that the disappearance of a pair of isopropyl radicals by a process other than combination leads on the average to the formation of more

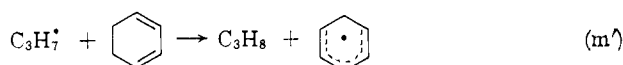
TABLE I
 THE GENERATION AND REACTIONS OF THE CYCLOHEXADIENYL RADICAL

Temp., °K.	Time, sec.	10 ⁻¹⁷ [D], [B], molecules/cm. ³		—10 ⁻¹² R(X), molecules/cm. ³ sec.—					M*	k ₃ /k ₂	10 ¹⁴ k _m / k ₂ ^{1/2} , (cm. ³ /molecule sec.) ^{1/2}	[k _d /k _c] ₃	[k _d /k _c] ₄	k _c ^I /k _c ^{II}
		CO	C ₃ H ₈	C ₃ H ₆	C ₆ H ₆	C ₆ H ₈	C ₆ H ₁₄							
347.5	3600	2.57	1.99	11.80	8.63	2.76	1.40	4.88	1.03	0.57	102	0.46	0.47	0.86
348.0	3600	2.54	1.65	10.12	6.14	2.34	0.81	2.66	(0.79)	(0.88)	112	0.35	(0.36)	0.88
352.9	3600	2.80	1.53	14.91	8.81	3.77	1.46	6.03	(0.90)	0.63	95	0.69	(0.90)	(0.60)
354.6	3600	2.88	2.04	17.13	12.80	3.84	2.21	6.25	0.98	0.61	132	0.49	0.58	0.88
359.4	3600	2.42	1.49	8.96	6.68	1.91	1.29	3.91	1.04	(0.49)	118	0.59	0.47	0.81
360.8	1800	2.69	1.69	5.91	5.51	1.22	0.78	1.50	1.05	(0.81)	175	0.29	(0.36)	(1.00)
368.0	3600	2.28	1.23	7.50	5.98	1.62	1.26	2.55	0.97	0.64	158	0.69	0.56	0.80
370.1	1800	2.94	1.08	10.57	8.21	2.32	2.00	4.00	0.97	0.58	177	(1.09)	(0.74)	0.82
375.9	3600	2.61	1.21	9.69	7.85	2.08	1.70	3.71	1.02	0.56	171	0.75	0.54	0.79
380.8	3600	2.57	1.65	10.70	9.87	1.80	1.92	2.90	1.01	0.62	189	0.46	0.47	0.90
394.0	3600	2.71	1.94	9.27	9.96	1.03	2.04	1.69	1.04	0.61	268	0.43	0.52	0.84
396.0	1800	1.97	0.99	7.14	7.14	1.36	1.17	2.00	(1.12)	(0.68)	337	0.35	0.51	(1.00)
402.7	1800	2.60	0.74	14.64	11.59	3.03	2.09	5.15	1.00	0.59	398	0.51	0.50	0.81
409.3	1800	2.57	0.64	17.73	13.14	4.10	2.31	6.64	0.99	0.62	437	0.58	0.58	0.93
Mean value, excluding the numbers in brackets									1.01	0.60		0.51	0.52	0.85
Limits of error at the 5% probability level									±0.05	±0.05		±0.30	±0.09	±0.09

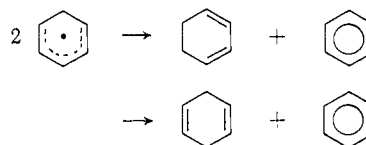
than a single propane molecule. Moreover, the ratio $M^* = \{R(C_3H_8) + R(C_6H_{14}) - R(C_6H_6)\} / R(CO) = 1.01 \pm 0.05$, indicating that the reaction which gives the supernumerary molecules of propane also yields an equal quantity of benzene. On the basis of the analytical and kinetic evidence, we propose that the generation and reactions of the cyclohexadienyl radical are adequately described by Scheme I.



The chromatograms clearly reveal the twin peaks corresponding to the adducts I and II and the single peak of benzene; but the peak corresponding to cyclohexadiene-1,3 is always absent, although it could have been detected very readily. Reaction e^I is therefore negligible. Moreover the ratio $R(C_3H_8)/R(C_6H_{14})$ gives the normal value of k_3/k_2 , indicating that the only appreciable source of propane is reaction 2, and thereby rendering both reactions e^I and e^{II} negligible. Further support for this mechanism was obtained from the photolysis of a gaseous mixture of diisopropyl ketone and cyclohexadiene-1,3, which generates the cyclohexadienyl radical by the reaction



The corresponding chromatograms for this system reveal peaks for I, II, and benzene, but the peak corresponding to cyclohexadiene-1,4 is always absent, although it could have been detected very readily. Reaction e^{II} is therefore negligible. Moreover the elimination of both reactions



results from the absence of the appropriate cyclohexadiene from the products of the two systems. The value $M^* = 1.01$ is also inconsistent with appreciable mutual combination or disproportionation of cyclohexadienyl radicals. The significant reactions of the cyclohexadienyl radical in this system are therefore reduced to three, and we shall show that their relative rates are given by the percentages beside the equations.

Propane is formed only in reactions 3, 4, m, and d, and therefore

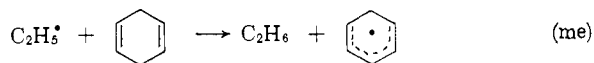
$$\begin{aligned}
 \frac{k_m}{k_2^{1/2}} &= \frac{\{R(C_3H_8) - R(C_3H_6) - R(C_6H_6)\}}{[B]R(C_6H_{14})^{1/2}} - \frac{k_4[D]}{k_2^{1/2}[B]} \\
 &= 10^{(-7.0 \pm 0.6)} e^{(-6.5 \pm 1.0)10^3/RT} (\text{cm.}^3/\text{molecule sec.})^{1/2} \quad (7)
 \end{aligned}$$

The associated Arrhenius plot is given as Fig. 1. Between 75 and 136° cyclohexadiene-1,4 exceeds diisopropyl ketone in reactivity toward the isopropyl radical by a factor ranging from 45 to 85. Accordingly the correction term of eq. 7 was often negligible and never exceeded 4% of the total, whereas at the highest temperature the consumption of cyclohexadiene-1,4 became appreciable, and an average value was used in the calculation.

The high reactivity of cyclohexadiene-1,4 is attributable to the increase in delocalization from the two isolated double bonds of the molecule to the five-carbon system of the radical. This increase is effec-

tive because the associated change in the geometry of the carbon skeleton is minor; the radical is known from its electron spin resonance spectrum to be flat,⁶ and although the molecule is boat-shaped, the rotational Raman spectrum reveals that the deviation from planarity is slight.⁷

This high reactivity has also been found in the system where the ethyl radical has been substituted for the isopropyl radical⁸



$$\frac{k_{\text{me}}}{k_{2\text{e}}^{1/2}} = 10^{(-7.3 \pm 0.1)e^{(5.8 \pm 0.1)10^3/RT}} \text{ (cm.}^3/\text{molecule sec.)}^{1/2}$$

The energy of activation is lower in the system involving the ethyl radical, in harmony with the greater strength of the carbon-hydrogen bond formed in this metathesis.

The chromatographic peaks for the 1-isopropylcyclohexadienes I and II can be identified by a comparison of the ratio of peak areas resulting from the interaction of the isopropyl radical with cyclohexadiene-1,4 and cyclohexadiene-1,3, respectively. Metathesis in each system forms the cyclohexadienyl radical, and so the ratio of peak areas from this source should be the same. Addition is appreciable only to cyclohexadiene-1,3; the resultant isopropylcyclohexenyl radical yields in turn I but not II by disproportionation. It was found that the earlier of the two peaks was relatively greater in the cyclohexadiene-1,3 system, so that the earlier peak was identified with I and the later peak with II. Thus the order of elution is the same for the cyclohexadienes and the isopropylcyclohexadienes; in each case the conjugated isomer appears first. Another peak would be expected in the cyclohexadiene-1,3 system; it would arise from 1-isopropylcyclohexadiene-1,3 formed by an alternative disproportionation of the isopropyl radical with the isopropylcyclohexenyl radical. Such a peak was found to appear a little before peaks I and II.

The Measurement of k_d/k_c and k_c^I/k_c^{II} .—The method of measurement of k_d/k_c rests upon two main assumptions: first that propane is formed only in reactions 3, 4, m, and d, and second, that the cyclohexadienyl radical disappears only by reactions c and d. Then if R_m is the rate of formation of the cyclohexadienyl radical, we have

$$R_c + R_d = R_m = R(\text{C}_3\text{H}_8) - R_3 - R_4 - R_d$$

$$k_d/k_c = R_d/R_c = \frac{R(\text{C}_6\text{H}_6)}{R(\text{C}_3\text{H}_8) - R(\text{C}_3\text{H}_6) - 2R(\text{C}_6\text{H}_6) - k_4[D](R(\text{C}_6\text{H}_{14})/k_2)^{1/2}}$$

(8)

All these quantities are measurable (the values of $k_4/k_2^{1/2}$ being interpolated from the results of photolysis of the pure ketone) and the direct application of eq. 8 gives $[k_d/k_c]_8 = 0.51 \pm 0.30$; median value 0.50. The precision of this method is not high because the

(6) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).

(7) B. J. Monostori and A. Weber, *J. Mol. Spectry.*, **12**, 129 (1964).

(8) A. C. R. Brown and D. G. L. James, unpublished results.

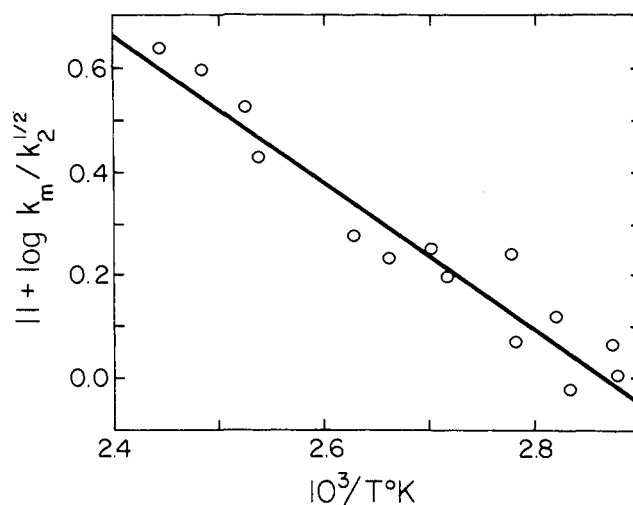


Fig. 1.—The formation of the cyclohexadienyl radical by the reaction $\text{C}_3\text{H}_7^\bullet + \text{C}_6\text{H}_6 \rightarrow \text{C}_3\text{H}_8 + \text{C}_6\text{H}_5^\bullet$.

denominator of the right-hand term is the difference of quantities of similar magnitude. It would be preferable to use the direct expression $k_d/k_c = R(\text{C}_6\text{H}_6) / \{R(\text{I}) + R(\text{II})\}$. This ratio of rates can be derived from the ratio of the corresponding areas (A) of the peaks of the chromatogram, if the appropriate calibrating factor can be determined. To do this, the quotient $Q = \{A(\text{I}) + A(\text{II})\} / A(\text{C}_6\text{H}_6)$ was found for each experiment, giving $Q = 2.3 \pm 0.4$, independent of temperature. Each value of Q was multiplied by the corresponding value of k_d/k_c calculated from eq. 8, to give the product $P = 1.18 \pm 0.20$, independent of temperature, with a median value of 1.17. The mean value was used as the calibrating factor, and values of k_d/k_c were calculated from the individual values of Q by the relation

$$k_d/k_c = 1.18/Q \quad (9)$$

yielding the result $[k_d/k_c]_9 = 0.52 \pm 0.09$, independent of temperature, with a median value of 0.52. Equations 8 and 9 give almost identical values of both the mean and the median, indicating that the assessment of the calibrating factor P is correct; the measurement of k_d/k_c by the comparison of peak areas is therefore the preferable and more precise method.

Assuming an equal sensitivity toward compounds I and II, we have placed

$$k_c^I/k_c^{II} = A(\text{I})/A(\text{II}) \quad (10)$$

$$= 0.85 \pm 0.09$$

The Mechanism of Combination and Disproportionation.—A comparison of the value $k_3/k_2 = 0.58$ with $k_d/k_c = 0.52$ might suggest a close similarity between the behavior of the isopropyl and cyclohexadienyl radicals in disproportionation. This similarity is illusory, as these radicals possess neither a common number of hydrogen atoms available for disproportionation nor a common number of sites available for combination. The importance of such considerations becomes clear when we consider the mechanism of the disproportionation and combination of two alkyl radicals. Bradley⁹ and Kerr and Trotman-Dickenson¹ have suggested that the paths of these two reactions must pass through a single common transition state. Thus the head-to-head interaction of two ethyl radicals

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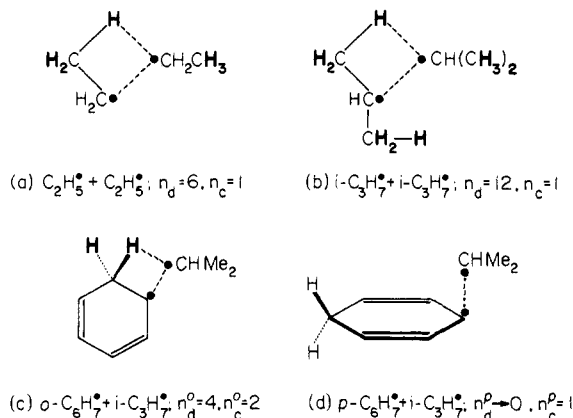


Fig. 2.—Models for the transition state for combination and disproportionation.

will form a butane molecule in a highly activated state, and this is the common transition state for both combination and disproportionation. The bending of the central carbon-carbon bond will be highly excited and will cause the type of interaction suggested by Fig. 2a. This represents the activated complex in terms of a four-center model, which can lead either to disproportionation by the transfer of the newly bonded hydrogen atom and the simultaneous cleavage of the central carbon-carbon bond, or to combination by the deactivation of the entire complex. Clearly, each hydrogen atom in the two methyl groups is equivalent, so that the number of hydrogen atoms available for disproportionation is given by $n_d = 6$, whereas the number of modes of association leading to combination is $n_c = 1$. The significant quotient for the interaction of two ethyl radicals is $(n_c k_d / n_d k_c) = 0.02$. Applying this interpretation to the interaction of two isopropyl radicals, we obtain Fig. 2b as a representation of the four-center activated complex, leading to the values: $n_d = 12$, $n_c = 1$, and $(n_c k_d / n_d k_c) = 0.05$. This theory of a common activated complex is supported by recent diagnostic experiments of Dixon, Stefani, and Szwarc, who have appended a critical discussion of its validity.¹⁰

The structure of the cyclohexadienyl radical has been deduced from the electron spin resonance spectrum of liquid⁶ and solid¹¹ cyclohexadiene-1,4 during irradiation with 2.8-Mev. electrons. The six carbon atoms are coplanar; the electron spin density at the methylene group is close to zero, and at the other positions is given by: *ortho*, 0.35; *meta*, -0.10; *para*, 0.50. These conclusions are confirmed by the electron spin resonance spectra of radicals formed in benzene by ionizing radiation¹¹⁻¹⁴ or hydrogen atom bombardment¹⁵ and are in general consistent with theoretical predictions of electron spin density in the cyclohexadienyl radical by molecular orbital and valence bond methods.¹⁶⁻¹⁸ Accordingly the single *para* and the two *ortho* positions are the only sites in the cyclohexa-

dienyl radical at which the initial interaction with the isopropyl radical is likely to occur. Let us first consider the nature of the interaction at each of these sites in isolation from the influence of the other two. The formation of a four-center complex by the interaction of an isopropyl radical with the cyclohexadienyl radical at one of the two *ortho* positions is represented in Fig. 2c; as only the methylene hydrogen atoms of the cyclohexadienyl radical are transferred, and as the *ortho* positions are equivalent, we have $n_c = 2$ and $n_d = 4$. It is difficult to see how a corresponding four-center complex could arise from interaction at the *para* position as the appropriate carbon-hydrogen distance is likely to be far too great, as in Fig. 2d; we therefore assign $n_d = 0$ and $n_c = 1$. The actual mechanism of interaction is probably related to the separate configurations of Fig. 2c and 2d, but the problem of superposition remains. The two extreme models for the over-all interaction would represent the three configurations as either independent or indistinguishable. In the former case the isopropyl radical would become specifically associated with one of the three sites in the cyclohexadienyl radical at an early stage; the activated complex would be quite strongly bonded and resemble the resultants rather than the reactants. If each configuration were to contribute independently and with equal weight, summation would give the effective values: $n_d = 4$, $n_c = 3$, and $(n_c k_d / n_d k_c) = 0.39 \pm 0.06$. On the other hand, the three separate configurations of the activated complex may be kinetically indistinguishable, possibly by the operation of the uncertainty principle.¹⁹ The isopropyl radical may become associated with the cyclohexadienyl radical as a whole without causing much perturbation of its electronic structure; such an activated complex would be rather loosely bonded and resemble the reactants fairly closely. The assignment of an effective value to n_c is more difficult in this case; it may well be 3, but clearly cannot be less than 1. Accordingly the minimum possible value of $(n_c k_d / n_d k_c)$ is 0.26 ± 0.04 , with $n_c = 1$ and $n_d = 2$.

The behavior of the system may lie between these extreme models, although we suggest below that the value of k_c^I / k_c^{II} indicates a loosely bonded activated complex. In any case, the minimum value predicted for $(n_c k_d / n_d k_c)$ is, at 0.26 ± 0.04 , substantially greater than the corresponding value of 0.050 ± 0.005 for the interaction of two isopropyl radicals, and shows that the tendency toward disproportionation is much greater for the cyclohexadienyl radical than for the isopropyl radical. The large delocalization energy of the product benzene presumably facilitates the disproportionation reaction of the cyclohexadienyl radical. This interpretation is supported by a parallel, but less complete, study of the system [ethyl + cyclohexadienyl]⁸ for which $k_d / k_c = 0.38 \pm 0.03$.

The arguments advanced above have been developed from the proposition that for closely related radicals the extent of disproportionation should be proportional to the number of β -hydrogen atoms n_d' .²⁰ This proposition has been recently challenged on the grounds that the quantity $k_d / n_d' k_c$ shows some scatter about a possibly characteristic value of 0.067, so that the quantity $0.067 n_d'$ deviates from the observed value

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of k_d/k_c for certain pairs of radicals.²¹ An alternative basis of correlation was inferred from a plot of $\log k_d/k_c$ vs. $S_d^\circ - S_c^\circ$, the difference in entropies of the products of disproportionation and combination. Most of the experimental points fall quite close to the straight line $\log k_d/k_c = 0.131(S_d^\circ - S_c^\circ) - 5.47$, confirming the general validity of the relationship. However, certain difficulties attend the application of this equation to the reactions of the cyclohexadienyl radical. First, $k_e/k_c = 0$ for both $(C_2H_5\cdot + C_6H_7\cdot)$ and $(C_3H_7\cdot + C_6H_7\cdot)$; even with realistic limits of error the deviation is likely to remain large. Second, the detailed application of the equation to the calculation of k_d/k_c for secondary radicals is no more successful than the use of $0.067n_d'$. Indeed, the greatest deviation is obtained with the only cyclic radical included in the correlation, the cyclopentyl radical, whereas $0.067n_d'$ predicts exactly the observed value of k_d/k_c for this radical. Third, the electron spin density distribution of the cyclohexadienyl radical differs fundamentally from that of any of the radicals included in the correlation, and presumably this difference should be represented in the equation by an additional term which normally vanishes. For these reasons we have concluded that the behavior of the system is described with least uncertainty by the expression $n_c k_d/n_d k_c$.

The ratio of the adducts is given by $k_c^I/k_c^{II} = 0.85 \pm 0.09$, significantly less than unity; on purely statistical grounds we should expect a value of 2. This ratio indicates the nature of the transition state. If the activated complex were to resemble the resultants rather than the reactants, then the course of the reaction should be strongly influenced by the electron localization energy of the cyclohexadienyl radical. Since this is least at the *ortho* positions, the formation of the conjugated adduct I would be favored and the

ratio should exceed 2. This is not the case. On the other hand, if the activated complex were to resemble the reactants closely, then the course of reaction should be dominated by free valence. The highest free valence on the cyclohexadienyl radical is found at the *para* position, and addition there would form the unconjugated adduct II. The predominance of II therefore indicates a loosely bonded transition state in which the electronic structure of the cyclohexadienyl radical has not been greatly perturbed. Free valence also appears to dominate the course of mutual disproportionation of cyclohexadienyl radicals in benzene solution,²² which yields cyclohexadiene-1,3 and cyclohexadiene-1,4 in the ratio of 1:2.7.

Conclusions

The interaction of the cyclohexadienyl radical with the isopropyl radical is described by the quotient $n_c k_d/n_d k_c \geq 0.26 \pm 0.04$. This value is unusually high for secondary radicals, and demonstrates that the course of the interaction may favor the formation of a product possessing a particularly high delocalization energy such as benzene. The value $k_c^I/k_c^{II} = 0.85 \pm 0.09$ indicates that the activated complex is loosely bonded and shows that the relatively small delocalization energy of a conjugated cyclohexadienyl ring is inadequate to influence the ratio of the adducts appreciably. The high reactivity of cyclohexadiene-1,4 toward metathesis is attributed to the favorable conjunction of a major increase in electron delocalization with a minor change in the geometry of the carbon skeleton.

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The Crystal and Molecular Structure of Tropone Iron Tricarbonyl

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The crystal structure of one form of $(C_6H_6CO)Fe(CO)_3$ has been determined by X-ray diffraction. The structure is found to be a π -complex with the iron atom bonded to four carbon atoms of the seven-membered ring.

Introduction

It has been shown that the reaction of iron dodecarbonyl with acetylene in inert solvent yields a number of organo iron carbonyls.¹ Among these is $(C_6H_6CO)Fe(CO)_3$, which is found to exist in at least two crystalline modifications. The compound can also be directly synthesized from tropone and $Fe_3(CO)_{12}$. It follows that $(C_6H_6CO)Fe(CO)_3$ is a complex made up of tropone bonded to an $Fe(CO)_3$ group by π -electrons.

One opinion arising in discussions of the bonding in this molecule is that the metal atom should overlap with the π -orbitals of all seven carbon atoms in the free

tropone ring. For example, in treating the bonding from a molecular orbital point of view, Brown² assumed that the iron atom is centrally located with respect to the double bonds of a planar tropone ring. On the other hand, Weiss and Hübel³ concluded that there is a localized double bond in the tropone ring. This they inferred from the fact that hydrogenation with H_2 under pressure and Pd at 40–70° produced cycloheptadienone-iron tricarbonyl.

This structure determination, along with the work on a triphenyl derivative by Smith and Dahl,⁴ clears up this

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