

can be added the error involved in the enthalpy as a function of temperature.

Conclusions that can be drawn from Table II concerning the differences between API values and those of this work are limited. Most values agree within the necessarily large error limits of the API values. The discrepancy in $\Delta S^\circ_{3,4}$ of about 1.0 e.u. probably means that the API data for the entropy of 1-butene are too low. The discrepancy in $\Delta S^\circ_{5,6}$, while smaller, also reflects errors in vibrational assignments, barriers to rotation, and experimental entropies.¹¹

(11) At the temperatures and pressures employed in the present work, corrections for gas nonideality are negligible.

A good deal of the impetus for the initial calorimetric and spectroscopic work on the hydrocarbons came from interest in discovering the magnitudes of the barriers to internal rotation. It appears now that this can be done with considerably more certainty by microwave measurements. In the case of the butenes these barriers are probably the most reliably known of the spectroscopic data. As a result it appears that the measurements of ΔS° from equilibrium studies, together with the known rotation barriers, could serve to fix better the low frequencies (*i.e.*, below 1000 cm^{-1}) of the butenes. In the temperature range investigated here these are the principal contributors to ΔS_{vib} .

[CONTRIBUTION FROM THE STANFORD RESEARCH INSTITUTE, MENLO PARK, CALIFORNIA]

Iodine-Catalyzed Isomerization of Olefins. II. The Resonance Energy of the Allyl Radical and the Kinetics of the Positional Isomerization of 1-Butene

BY KURT W. EGGER, DAVID M. GOLDEN, AND SIDNEY W. BENSON

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The kinetics of the iodine atom catalyzed isomerization of 1-butene to 2-butene have been studied over a wider temperature range and with greater precision than previously reported. The activation energy for the iodine atom attack on 1-butene is 12.4 ± 0.3 kcal./mole. When subtracted from the value 25.0 ± 0.5 kcal./mole for the analogous reaction of iodine atom with propane, this yields 12.6 kcal. for the resonance energy in 1-butene if the activation energies for the back reactions are assumed equal. The uncertainty from all sources is ± 1 kcal. The agreement with earlier work by Benson, *et al.*, is excellent and is confirmed by less direct studies of the pyrolysis of vinylcyclopropane and vinylcyclobutanes. The formation of small amounts of butadiene and other side products has been detected. It is shown that these do not alter the basic simplicity of the system.

Introduction

A preliminary kinetic study of the iodine atom catalyzed positional isomerization of 1-butene has been previously reported by Benson, *et al.*¹ In the course of repeating this work to verify the operation of a new system in a new laboratory, small errors in plotting and calculation were found in the work of Benson, *et al.* In addition, the more sensitive pressure-measuring device and analytical techniques used here led to the observation of the formation of small amounts of butadiene and other side products unnoticed by these workers (see Appendix). In view of the interest in having a reliable measure of the allylic resonance energy, kinetic studies of the iodine-catalyzed isomerization of 1-butene to 2-butene were made in the temperature range of 465 to 543°K. with an 18-fold variation in surface-to-volume ratios.

Since the completion of this work Ellis and Frey² have questioned the "low" value of the allylic resonance energy deduced by Benson and co-workers from their measurements and verified in this work. In this connection the various values and their sources are discussed.

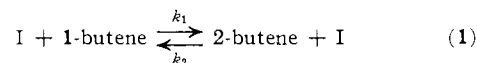
Experimental

The techniques are similar to those of Benson, *et al.*, and have been described in great detail in a previous publication.³

Results

Following the reasoning of Benson and co-workers the kinetic behavior of the iodine atom catalyzed posi-

tional isomerization is represented by the reversible reaction



This rests on the assumption that the *cis* and *trans* isomers of 2-butene are always in equilibrium. Measurements⁴ show that this is not always the case, but that the validity of the assumption is upheld throughout the experiments reported here.

The rate law is (1-butene = B_1 ; 2-butene = B_2)

$$-\frac{d(B_1)}{dt} = k_1(I)(B_1) \left[1 - \frac{(B_2)/(B_1)}{K_{1,2}} \right] \quad (2)$$

The equilibrium constant $K_{1,2} = k_1/k_2$ is known from earlier independent measurements.³ Using the stoichiometric relationship $(B_1) + (B_2) = (B_1)_0$ and setting $(I) = K_{I_2}^{1/2}(I_2)^{1/2}$ (where K_{I_2} is the equilibrium constant for the dissociation of I_2)⁵ yields upon integration of (2)

$$k_1 = - \frac{K_{1,2}/(1 + K_{1,2})}{K_{I_2}^{1/2}(I_2)^{1/2}t} \left(\frac{1 + K_{1,2}}{K_{1,2}} \right) \quad (3)$$

In Table I the values of k_1 obtained from eq. 3 are listed together with other pertinent information for each run.⁶ As can be seen, the form of the derived rate law is obeyed well over a tenfold range of I_2 pressures, a ninefold range in $(B_1)_0$ pressures, and a tenfold range in $(B_1)_0/(I_2)$.

(4) S. W. Benson, K. W. Egger, and D. M. Golden, *ibid.*, submitted for publication.

(5) JANAF Interim Thermochemical Tables (Dow Chemical Co., Midland, Mich., 1960).

(6) In those runs where B_2 was the starting material an equilibrium mixture of *cis*- and *trans*-2-butene was used and eq. 3 was suitably altered.

(1) S. W. Benson, A. N. Bose, and P. Nangia, *J. Am. Chem. Soc.*, **85**, 1388 (1963).

(2) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 959 (1964).

(3) D. M. Golden, K. W. Egger, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5416 (1964).

TABLE I
 KINETIC DATA FOR THE POSITIONAL ISOMERIZATION OF 1-BUTENE

| Temp., °K. | Run no. ^a and vessel | Time, min. | [I ₂] ₀ , mm. | [I ₂] _{eff.} ^b , mm. | [B] ₀ B ₁ , B _t , B _c , mm. | K _{1,2} ^{1/2} × 10 ⁴ , | | B ₁ /(B ₁) ₀ ^d [or B ₂ /(B ₂) ₀] | k ₁ | |
|---------------|------------------------------------|---------------|---|---|--|---|-------------------------------|---|----------------|--------------------|
| | | | | | | mm. ^{1/2} | K _{1,2} ^c | | | |
| 465.3 | 33 | 132 | 25.7 | 25.5 | 1 | 26.5 | 0.3876 | 6.99 | 0.925 | 3.06 |
| | 46 | 722 | 12.8 | 12.3 | 1 | 35.8 | | | 0.725 | 3.32 |
| | 47 | 305 | 30.2 | 29.8 | 1 | 26.8 | | | 0.824 | 3.07 |
| | 48 | 1010 | 46.6 | 46.1 | t + c | 49.8 | | | [0.919] | 3.10 |
| 468.3 | 55 p | 644 | 12.4 | 11.4 | 1 | 48.5 | 0.430 | 6.90 | 0.608 | 5.57 |
| | 56 p | 202 | 44.7 | 44.1 | 1 | 53.7 | | | 0.770 | 4.65 |
| | 57 p | 247 | 18.9 | 18.0 | 1 | 143.3 | | | 0.830 | 4.19 |
| | 58 p | 994 | 4.3 | 3.9 | 1 | 27.6 | | | 0.628 | 5.72 |
| | 59 p | 937 | 5.4 | 4.9 | 1 | 163.6 | | | 0.645 | 5.11 |
| 467.8 | 77 p | 214 | 30.9 | 28.1 | 1 | 55.2 | 0.4312 | 6.83 | 0.784 | 5.08 |
| 484.5 | 31 | 132 | 25.6 | 24.7 | 1 | 31.4 | 0.848 | 6.32 | 0.841 | 4.73 |
| 484.9 | 53 p | 121 | 29.9 | 28.4 | 1 | 38.1 | 0.862 | 6.30 | 0.747 | 5.39 |
| | 54 p | 70 | 31.9 | 30.7 | 1 | 52.6 | | | 0.841 | 5.30 |
| 510.5 | 9 | 240 | 12.1 | 11.6 | 1 | 36.0 | 2.241 | 5.49 | 0.271 | 9.15 |
| | 10 | 370 | 11.9 | 11.0 | 1 | 35.6 | | | 0.195 | 9.32 |
| | 11 | 360 | 18.4 | 17.8 | 1 | 40.7 | | | 0.181 | 8.55 |
| | 12 | 525 | 11.7 | 10.5 | 1 | 42.3 | | | 0.172 | 8.59 |
| | 14 | 118 | 19.7 | 18.6 | 1 | 23.1 | | | 0.398 | 9.25 |
| | 15 | 94 | 25.0 | 23.9 | 1 | 42.9 | | | 0.420 | 9.50 |
| | 16 | 70 | 25.0 | 23.3 | 1 | 194.4 | | | 0.515 | 9.55 |
| | 17 | 50.5 | 24.8 | 23.6 | 1 | 38.8 | | | 0.621 | 9.18 |
| | 18 | 40 | 24.8 | 23.8 | 1 | 37.3 | | | 0.678 | 9.32 |
| | 543.0 | 25 | 40.5 | 15.7 | 13.5 | 1 | 37.9 | 6.581 | 4.73 | 0.262 |
| 26 | | 50 | 15.0 | 13.8 | 1 | 33.2 | | | 0.241 | 17.10 |
| 27 | | 40 | 10.9 | 10.0 | 1 | 27.7 | | | 0.300 | 18.98 |
| 28 | | 31 | 3.4 | 2.9 | 1 | 33.3 | | | 0.561 | 18.04 |
| 29 | | 15 | 3.9 | 3.4 | 1 | 31.2 | | | 0.731 | 17.94 |
| 30 | | 41.5 | 4.5 | 3.8 | 1 | 39.5 | | | 0.432 | 18.20 |
| 541.9 | | 52 p | 31 | 4.6 | 3.7 | 1 | 41.1 | 6.375 | 4.75 | 0.494 |
| 572.2 | 71 p | 12.1 | 2.7 | 0.99 | t + c | 78.9 | 15.58 | 4.25 | [0.878] | 44.46 ^e |
| | 72 p | 10 | 1.8 | 0.89 | t + c | 27.4 | | | [0.904] | 39.29 ^e |
| | 73 p | 8.5 | 1.2 | 0.33 | 1 | 36.2 | | | 0.689 | 51.85 ^e |
| | 74 p | 5 | 4.2 | 2.60 | 1 | 42.6 | | | 0.624 | 40.36 ^e |
| | 75 p | 6.5 | 4.0 | 1.88 | 1 | 50.9 | | | 0.569 | 44.44 ^e |

^a p = packed vessel, no marks = unpacked vessel. ^b [I₂]_{eff} = effective iodine pressure, calculated from the initial pressure [I₂]₀, corrected for iodine changes during the reaction. ^c K_{1,2} = K_{3,4}[1 + 1/K_{5,6}] where K_{3,4} is the equilibrium constant for the reaction B₁ $\xrightleftharpoons[k_4]{k_3}$ B_t and K_{5,6} is the equilibrium constant for the geometrical isomerization B_c $\xrightleftharpoons[k_6]{k_5}$ B_t. ^d B₁/(B₁)₀ = 1/[1 + ((B_t/B₁)_{final} × (1 + 1/K_{1,2}))]. ^e These results are entered for reason of completeness only and they are not weighed for computing the Arrhenius parameters in Fig. 1. Compare text and columns 4 and 5.

Errors in k₁ vary linearly with errors in the butene analysis and with any deviation from the assumed stoichiometry due to side reactions. Changes in initial iodine pressure enter to the 1/2 power. The only significant, though still small, side reaction is the production of butadiene (see Appendix). Errors introduced in (I)₀ and (B₁)₀ due to this reaction are in opposite directions. Rate constants were calculated using an effective iodine pressure [I₂]_{eff} obtained by subtracting a time average of the iodine loss during a run from the initial iodine pressure [I₂]₀ and by adding an appropriate amount for the sweeping of iodine into the vessel from the dead space during the admission of the butene. (The difference in the slopes of Arrhenius plots using [I₂]₀ and [I₂]_{eff} is 3%.)

At 572°K. where iodine pressures of only a few torr were used in order to keep the rate of reaction 1 within measurable bounds, the decrease in iodine pressure due to butadiene formation was between 50 and 80% in a matter of seconds. [I₂]_{eff} was calculated for this temperature by simply subtracting the large initial iodine loss, but the value of [I₂]_{eff} is so uncertain that experiments at this temperature were not used to determine Arrhenius parameters.

Corrections in (B₁)₀ were not made as there was usually more butene than iodine and the per cent change in (B₁)₀ is quite small.

In Fig. 1 are plotted log k₁ values vs. 1/T (°K.) from this work and from the data of Benson, *et al.*⁷ A small surface effect is noticeable at 470°K. An 18-fold increase in surface-to-volume ratio enhances the rate by less than 50%. At higher temperatures no increase in rate was observed.

The Arrhenius parameters for the expression

$$\log k_1 = \log A_1 - E_1/\theta \quad (4)$$

where $\theta = 2.303RT$ in kcal./mole are

| | log A ₁ (1./mole/sec.) (The error limits are maximum deviations) | E ₁ (kcal./mole) |
|------------------------------------|--|-----------------------------|
| This work | 9.0 ± 0.3 | 12.4 ± 0.6 |
| Benson, <i>et al.</i> ⁷ | 8.8 ± 0.5 | 11.7 ± 1.2 |

Discussion

The allylic resonance energy is defined as the difference in dissociation energies between a C-H bond conjugated with a double bond and the similar bond in

(7) The data of Benson, Bose, and Nangia are corrected for the newer JANAF values of K_{1,2} and for a calculational error.

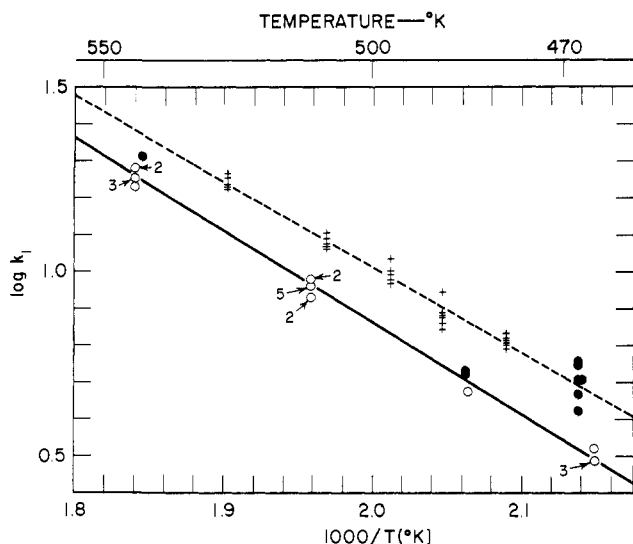


Fig. 1.—Plot of $\log k_1$ (units of $\text{mm.}^{-1} \text{min.}^{-1}$) for the positional isomerization of 1-butene vs. the reciprocal of the temperature ($^{\circ}\text{K.}$): + ref. 1, \circ unpacked vessel, \bullet packed vessel. (Numbers indicate overlapping points.)

a saturated paraffin at the same temperature. On the assumption that the dissociation energy of the secondary C-H bond in *n*-butane is the same as that in propane

$$\text{allylic resonance energy} = D^{\text{T}}(\text{secondary C-H})_{\text{propane}} - D^{\text{T}}(\text{secondary C-H})_{1\text{-butene}} \quad (5)$$

This work yields the activation energy (E_1) for the hydrogen abstraction from 1-butene by an iodine atom. The difference between E_1 and the activation energy (E_b) for the back reaction (attack on HI by a methyl allyl radical) is equal to the difference between $D^{\text{T}}(\text{secondary C-H})_{1\text{-butene}}$ and $D^{\text{T}}(\text{H-I})$.

Nangia and Benson⁸ have studied the kinetics of secondary hydrogen atom abstraction from propane by iodine atoms in the same temperature range as this work and have obtained E_1' in analogy to E_1 . Their value is $E_1' = 25.0 \pm 0.5$ kcal./mole. Therefore

$$\text{allylic resonance energy} = (E_1' - E_1) + (E_b - E_b') \quad (6)$$

on the assumption that the activation energy for HI attack on methyl allyl radicals is the same as that for HI attack on isopropyl radicals^{8,9} ($E_b = E_b'$) and the allylic resonance energy is 12.6 ± 0.8 kcal./mole. This value includes the uncertainties in E_1 and E_1' as well as an assigned error of ± 0.5 kcal./mole for the uncertainty in the assumption that $E_b = E_b'$.

If the error limits are broadened to take into account any possible difference between the secondary C-H bonds in propane and *n*-butane, the uncertainty in the allylic resonance energy should not be more than ± 1 kcal./mole.

The value from Benson and co-workers is 13.3 ± 1.3 kcal./mole.

Ellis and Frey,² comparing the activation energies for the isomerization of 1,1-dimethylcyclopropane to methylbutene and 1-methyl-1-vinylcyclopropane to

(8) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964).

(9) (a) S. W. Benson and H. E. O'Neal, *J. Chem. Phys.*, **36**, 2196 (1962);

(b) S. W. Benson and H. E. O'Neal, *ibid.*, **37**, 540 (1962); (c) H. Teranishi

and S. W. Benson, *J. Am. Chem. Soc.*, **85**, 2887 (1963); (d) D. B. Hartley and

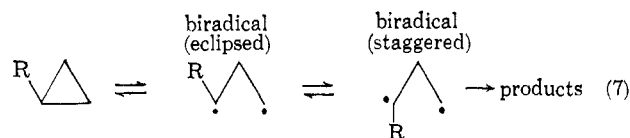
S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963).

1-methylcyclopentene, deduce a value for the allylic resonance energy of 13.2 kcal./mole. This value has an uncertainty of about ± 1 kcal./mole and is in excellent agreement with the value of 12.6 ± 1 kcal./mole reported here.

Despite this apparent agreement of two values obtained from widely different studies, one on radicals and the other on biradicals, Ellis and Frey have voiced some reservations concerning their own experimental estimates of the allyl resonance energy. Their reservation is based on an analogy concerning the strain energy in cyclopropane. They note that while the strain energy in cyclopropane is estimated at 28 kcal.,¹⁰ the activation energy for opening the ring, 63 kcal., is only 19 kcal. less than the normal $>\text{C}-\text{C}<$ bond strength of 82 kcal. Hence not all of the strain energy is relieved in reaching the transition state for ring opening. If this is the case, then why should one expect all of the allylic resonance energy to be developed in the transition state? On this basis they decide that it is more likely that only two-thirds or perhaps three-fourths of the allylic resonance energy should be realized in the transition state and hence the true value for this energy should be perhaps three-halves or four-thirds of their observed 13 kcal., or about 17 kcal., which is closer to a rather crudely calculated quantum-mechanical value¹¹ of 17 ± 5 kcal.

Such an argument based on analogy cannot be taken very seriously unless it can be shown that the analogy is relevant. In this particular case of ring opening Benson¹⁰ has proposed that the residual 8 kcal. of strain energy in the cyclopropane transition state arises from the unfavorable eclipsed configuration of neighboring groups and thus has very little to do with the broken C-C bond. If this is the case it has little bearing on the allylic resonance energy in the transition state which is not involved in the problem of eclipsing of ring hydrogen atoms:

This division of the strain energy into ring strain and eclipsing strain was first proposed by Seubold,¹² who, however, did not consider the latter for cyclopropane and estimated it at 6 kcal. for cyclobutane. Present knowledge of these two structures, the latter being nonplanar, would estimate eclipsing energy at about 6 kcal. for cyclopropane and somewhat less for cyclobutane. On this basis, Benson's model for the pyrolysis of small rings would be as follows



The transition state would correspond to the eclipsed form of the biradical which would be some 6-8 kcal. in energy above the ground-state, staggered biradical. The allylic resonance of a group R with the biradical could be fully developed in either state and on this basis the result of Ellis and Frey is taken as excellent confirmation of the result obtained here with the mono-radical.

(10) S. W. Benson, *ibid.*, **34**, 521 (1961).

(11) J. L. Franklin and F. H. Field, *J. Am. Chem. Soc.*, **75**, 2819 (1953).

(12) F. H. Seubold, Jr., *J. Chem. Phys.*, **21**, 1616 (1953).

Since the original preparation of this paper, however, two further studies have lent even more striking support to our proposed value of the allylic resonance energy. Hammond, *et al.*,¹³ reported the thermal Cope rearrangement of several vinyl-substituted cyclobutanes. For the first-order cleavage of the carbon bond between the substituents in *trans*-divinylcyclobutane they have reported an activation energy of $\Delta H^* = 34.0$ kcal./mole. At a mean temperature $\langle T \rangle = 448^\circ\text{K}$. we calculate $E = \Delta H^* + RT = 34.0 + 0.9 = 34.9$ kcal./mole. This value is to be compared with the activation energy of 61.6 kcal./mole for the cleavage of the same bond in 1,2-dimethylcyclobutane, as reported by Gerberich, *et al.*¹⁴ This leads to an allylic resonance energy of $(61.6 - 34.9)/2$ or 13.4 kcal.

Trecker *et al.*,¹⁵ have reported on similar studies involving the rearrangement of *trans*-1,2-divinyl-1,2-dimethylcyclobutane. This reaction also proceeds through the formation of a biradical intermediate formed upon opening of the C₁-C₂ bond, and the activation energy is 32.2 kcal./mole. There are no data available on the apparent saturated homolog, the 1,1,2,2-tetramethylcyclobutane. It is, however, reasonable to use the value for 1,2-dimethylcyclobutane. Two opposing effects arise from the addition of the two extra methyl groups; one is the weakening of the C-C ring bond and the other is the stabilization of the butane ring. These should tend to cancel each other. If they do, then we find $(61.6 - 32.2)/2 = 14.7$ kcal./mole allylic resonance energy. Considering the uncertainty connected with such calculations, the agreement of these results is quite good.

Although the strain energies in the cyclopropane and cyclobutane rings are nearly the same, the residual strain energy in the cyclobutane transition state is only 3 to 4 kcal.^{10,16} markedly different from the 8 to 9 kcal. estimated for the cyclopropane system. This lends support to the proposal that this extra strain is associated with eclipsed configurations and makes quite tenuous the analogy employed by Ellis and Frey.²

Szwarc, *et al.*,¹⁷ have reported the measurement of the C-C bond-dissociation energy in 1-butene by pyrolyzing gaseous 1-butene in a stream of toluene. The unreliability of this flow system technique for measuring the bond dissociation energy $D(\text{C}_6\text{H}_5\text{CH}_2 \cdots \text{H})$ in toluene^{18a} and $D(\text{allyl}-\text{H})$ in propylene^{18b} and the ill-defined stoichiometry of the system lead to the conclusion that the reported value of 21 ± 2 kcal./mole for the allylic resonance energy is a serious overestimate.

Gordon, *et al.*,¹⁹ have reported an activation energy of 31.8 ± 3.6 kcal./mole for hydrogen atom abstraction by allyl radicals from cyclopentane. This value, together with an assumed value of 10 kcal. for the back reaction, can be used to estimate a crude value of 22 ± 4 kcal. for the heat of reaction. Combining

this with a value of 95 kcal. for the secondary C-H bond in cyclopentane yields a value of 73 ± 4 kcal. for the primary C-H bond in propylene. This is lower by about 5 kcal. than any value which has been proposed by more direct measure for this bond strength and would imply an allyl resonance energy of 25 ± 4 kcal. However, the data on which the first value is based are very suspect and the system is much more complex than the authors have indicated. It is doubtful if the reactions on which the 31.8 kcal. is based are the proper ones, a number of quite important reactions having been omitted. Finally, it can be shown that the data are not self-consistent.²⁰

The present values of the allyl resonance energy appear to be the most direct and least subject to experimental uncertainty. They also show unanticipated agreement in strikingly different studies. They do, however, rest on an assumption ($E_b = E_b'$) which, while very plausible from our past experience with similar radical + HI reactions, has not been tested directly. Since it is not likely that $E_b < E_b'$, the present value of the resonance energy is most probably also a minimum value.

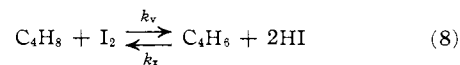
Appendix

The iodine-catalyzed isomerization of butenes is basically a very clean reaction. There are, however, two interesting and distinctly recognizable side reactions which produce small amounts of butadiene and *n*-butane, respectively, depending on the experimental conditions used. Within the large experimental error attached to g.l.c. analysis of such small amounts, all the experiments listed in Table I give rise to the quantities in Table II.

TABLE II

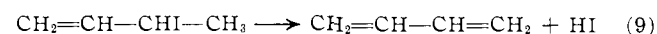
| Temp., °K. | Butadiene in % of the total C ₄ -hydrocarbon | Butane | log K _A , mm. |
|---------------|--|--------|-----------------------------|
| 465 | 0.5-1.9 | 0-0.1 | -2.57 |
| 511 | 1.9-5.0 | 0-0.2 | -1.42 |
| 543 | 1.9-6.8 | 0-0.2 | -0.71 |
| 572 | 2.4-3.6 | 0-0.1 | -0.13 |

The butadiene formation can be written as



The measured changes in iodine concentrations and total pressure during the early stages of the positional isomerization of 1-butene suggest that equilibrium (8) is established within seconds at 572°K ., within several minutes at 543°K ., and in the order of hours at 465°K ..

About the only reasonable source of butadiene is the unimolecular elimination reaction



This means that this reaction is considerably more rapid than the corresponding elimination from *i*-PrI²¹ or *sec*-BuI.²² The rapid rate can be attributed partly to the lower endothermicity of the reaction (~ 3 kcal./mole) and partly to the neighboring group effect of the very polarizable vinyl group. This would be consistent with the theoretical model for these

(20) From the reported products it can be inferred that the steady-state (allyl/methyl) ratio is $\sim 10^6$. This would imply rather large and unaccounted allyl-allyl termination reactions.

(21) H. Teranishi and S. W. Benson, *J. Chem. Phys.*, **41**, 2946 (1964).

(22) P. Nangia and S. W. Benson, *ibid.*, **41**, 2773 (1964).

(13) G. S. Hammond and C. H. DeBoer, *J. Am. Chem. Soc.*, **86**, 899 (1964).

(14) H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 4884 (1961).

(15) D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

(16) P. S. Nangia and S. W. Benson, *J. Chem. Phys.*, **38**, 18 (1963).

(17) M. Szwarc and A. H. Sehon, *ibid.*, **18**, 237 (1950).

(18) (a) S. W. Benson and J. H. Buss, *J. Phys. Chem.*, **61**, 104 (1957);

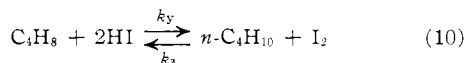
(b) A. Amano and M. Uchiyama, *ibid.*, **68**, 1133 (1964).

(19) A. S. Gordon, S. R. Smith, and J. R. McNesby, *J. Am. Chem. Soc.*, **81**, 5059 (1959).

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.



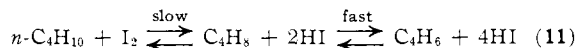
(23) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963).

(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."

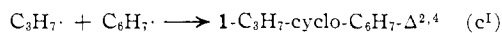
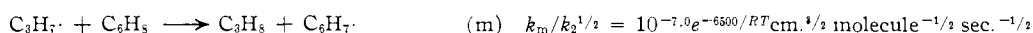
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A Kinetic Study of the Cyclohexadienyl Radical. I. Disproportionation and Combination with the Isopropyl Radical

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

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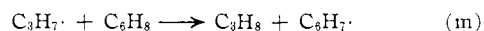
The kinetics of the generation and reactions of the cyclohexadienyl radical with the isopropyl radical may be described by the equations



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.

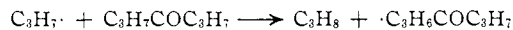
Among the alkyl radicals, the ratio of disproportionation to combination normally increases with an increasing degree of substitution at the reactive carbon atom. This trend is illustrated by the values¹ of k_d/k_c for the series $[\text{CH}_3\text{CH}_2\cdot, 0.14] < [(\text{CH}_3)_2\text{CH}\cdot, 0.65] < [(\text{CH}_3)_3\text{C}\cdot, 4.2]$. 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

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(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).