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Reaction of Cyclohexane with Mercury-6($^3P_1$) Atoms*

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An investigation has been made of the mercury-6($^3P_1$)-photosensitized decomposition of cyclohexane at 29.30±0.01°C, under static conditions. The products of the reaction are hydrogen, bicyclohexyl, and cyclohexene, in order of decreasing importance. The mean quantum yields of cyclohexane disappearance, hydrogen formation, and cyclohexene formation were found to increase slightly with increasing substrate pressure; at 90-mm cyclohexane pressure, the values are 0.83, 0.43, and 0.03, respectively. Extrapolation to initial conditions of data on the variation of mean quantum yield with time at constant substrate pressure gave 0.55 for the initial quantum yield of hydrogen formation, and 0.17 for cyclohexene formation, independent of substrate pressure. From the foregoing initial quantum yield data, taken in conjunction with the stoichiometry of the reaction, a value of 0.93 was obtained for the initial quantum yield of cyclohexane consumption.

Absence of hexane, dodecanes, *n*-hexylcyclohexane, and low molecular weights products was taken as evidence of the stability of the cyclohexane ring during reaction.

The results of the investigation can be adequately accounted for by the following simple mechanism:

(1) cyclo C_6H_{12}+Hg 6($^3P_1$)→cyclo C_6H_{11}+H+Hg 6($^1S_0$),

(2) H+cyclo C_6H_{12}→H_2+cyclo C_6H_{11},

(3) 2 cyclo C_6H_{11}→cyclo C_6H_{10}+cyclo C_6H_{12},

(4) 2 cyclo C_6H_{11}→bicyclo $C_{12}H_{22}$,

(5) H+cyclo C_6H_{10}→cyclo C_6H_{11}.

Steps (1) to (4) describe the reaction under initial conditions.

From the initial quantum yield data the ratio k_4/k_3, the ratio of the rates of recombination to disproportionation for cyclohexyl radicals, was evaluated at 2.2. In short, recombination is approximately twice as fast as disproportionation for cyclohexyl radicals.

INTRODUCTION

In the study of the reactions of hydrocarbons with Hg-6($^3P_1$) atoms in the gas phase, a great deal of evidence has now accumulated which points fairly unequivocally to the fact that the primary process involves C—H bond scission exclusively. Investigations on the cycloparaffins in this laboratory indicate that they also conform to the aforementioned generalization.[1–3] Earlier published data on the complex cyclopropane reaction led to the conclusion that ring cleavage occurred in the primary process.[4,5] However a detailed study[6] which has recently been completed on this reaction suggests that the seemingly exceptional behavior of this molecule arises from the rapid isomerization of cyclopropyl radicals formed in the primary process, rather than by primary C—C bond rupture.

The present investigation on cyclohexane formed part of our general program on the mercury-6($^3P_1$) reactions of the cycloparaffins. The results follow.

EXPERIMENTAL

The general experimental technique used in this series of investigations on the cycloparaffins has been previously described.[2,7]

The cylindrical fused quartz reaction cell was 8.5 cm long and 5 cm in diameter. The thermostat, wherein the cell was immersed, was maintained at 29.30±0.01°C. The connecting tubing of the reaction system was constructed entirely of heavy-walled 3-mm i.d. capillary, to minimize the effects of ambient temperature fluctuations on the pressure readings. The Pearson differential manometer was maintained at the same temperature as the reaction cell.[2] Condensable products for mass spectral analysis and chemical characterization were removed from the system by freezing them in a small detachable finger trap which was connected to the reaction cell.

The resonance lamp[2] was operated from a Sola Luminous Tube Transformer supplying 3000 v at 30 ma. Primary input to the lamp transformer was stabilized as before with a Sola Constant Voltage Transformer.

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[1] Allen, Kantro, and Gunning, J. Am. Chem. Soc. **72**, 3588 (1950).

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[3] D. L. Kantro and H. E. Gunning, J. Chem. Phys. (to be published).

[4] H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. **17**, 351 (1949).

[5] R. Scott and H. E. Gunning, J. Phys. Chem. **56**, 156 (1952).

[6] Ford, Mori, and Gunning (unpublished work).

[7] G. A. Allen and H. E. Gunning, J. Chem. Phys. **16**, 1146 (1948).

The 1849A radiation from the lamp was removed with a Vycor 7910 filter.

For the generation of larger quantities of condensable products, an auxiliary apparatus was employed similar to that described in our work on the cyclopropane reaction.[5] Here the tubular reaction cell, which was inserted axially through the coils of the quartz resonance lamp, was fashioned of 30-mm i.d. Vycor 7910 tubing.

The cyclohexane used in the investigation was National Bureau of Standards sample No. 209a-8s. Stated limits of impurity were 0.010±0.006 mole percent. The ampoules of cyclohexane were connected to the reaction system, via Fugassi valves.[2]

The hydrogen (Mathieson Reagent Grade) was 99.9 percent pure. The cyclopropane (Ohio U.S.P. Grade) used in the actinometric runs was purified by several trap-to-trap distillations. Mass spectral analysis of the purified material gave cyclopropane 99.9 percent, propane 0.1 percent.

The bicyclohexyl used was obtained by fractional distillation of Monsanto Technical Grade material on a Podbielniak Hypercal column. Density, refractive index, and boiling point of the purified material were in accordance with reported values on this compound.

The *n*-hexylcyclohexane was synthesized by standard methods and purified in a similar manner to the bicyclohexyl.

The mass spectral data were obtained with a Consolidated Engineering Model 21–103 instrument. For the infrared data a Perkin-Elmer double-beam instrument was employed.

TABLE I. Quantum yield of pressure decrease at various initial pressures of cyclohexane.

Initial cyclohexane pressure mm	Duration of exposure min	Quantum yield of pressure decrease mole/einstein
3.6	20	0.048
10.3	50	0.172
10.3	60	0.160
15.0	60	0.216
18.7	30	0.25
26.7	48	0.31
27.6	34	0.35
28.0	60	0.32
28.6	60	0.31
39.6	30	0.34
40.8	30	0.40
50.4	30	0.46
51.6	60	0.48
52.0	30	0.46
54.0	30	0.50
61.8	50	0.58
62.0	60	0.60
64.5	30	0.68
66.0	30	0.63
69.0	30	0.63
70.6	60	0.70
74.1	30	0.70
77.5	30	0.81
78.6	156	0.83
79.2	60	0.84
85.1	60	0.93

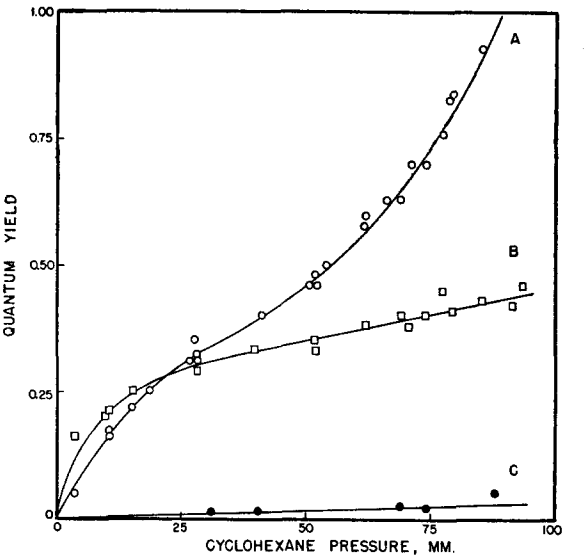

FIG. 1. Curve *A*, quantum yield of pressure decrease. Curve *B*, quantum yield of hydrogen formation. Curve *C*, quantum yield of cyclohexene formation.

RESULTS

The reaction is pressure-decreasing, with the rate of pressure decrease reaching a maximum and constant value after two to three minutes of exposure. After approximately thirty minutes of exposure, the rate was observed to fall off with increasing rapidity. During the irradiation, minute droplets of a colorless liquid were noted to form on the incident face of the cell. The pressure decrease is due to the condensation of this product.

In order to ascertain whether the falling-off in the rate of pressure decrease, upon prolonged exposure, arose from absorption of the incident radiation by the liquid product, several runs were carried out as follows: at the end of a run, the system was evacuated, but the cell was not removed for cleaning. A new charge of cyclohexane was admitted at the same pressure as in the preceding run, and the lamp was turned on. For this run the rate of pressure decrease was found to coincide with the final rate of pressure decrease in the clean cell. As an example, at a pressure of 45 mm of cyclohexane, the rate of pressure decrease, during the first thirty minutes of exposure in a cleaned cell, was 0.233 mm/min. After an hour of exposure, the slope of the pressure-time curve corresponded to 0.164 mm/min. When the run was resumed with a fresh charge of cyclohexane, the constant rate of pressure decrease was 0.168 mm/min. From data such as these it was concluded that the reduced rate at long exposures could be attributed to the screening effect of the condensed product.

The light intensity was checked at regular periods during the course of the investigation, using the cyclopropane reaction as the actinometer.[2] The mean value of the light intensity at 2537A was $2.5\pm0.05\times10^{-6}$ einstein/min.

TABLE II. Mean quantum yield of hydrogen formation as a function of cyclohexane pressure for runs of 30 to 60 minutes' duration.

P_0 mm	Q_{H_2}	P_0 mm	Q_{H_2}
3.6	0.16	54.0	0.41
9.6	0.20	62.0	0.38
10.3	0.21	69.0	0.40
10.3	0.20	70.5	0.38
15.0	0.25	74.1	0.40
28.0	0.29	77.5	0.45
28.5	0.29	79.2	0.41
39.6	0.33	85.1	0.43
51.6	0.35	91.2	0.42
51.9	0.33	93.3	0.46

The data on the quantum yield of pressure decrease as a function of initial substrate pressure are given in Table I and Fig. 1.

Analysis of the gas, noncondensable in liquid nitrogen, remaining after reaction, showed that it consisted of at least 99 percent mole percent hydrogen. The average rate of hydrogen formation was determined as a function of both cyclohexane pressure and of duration of exposure. The data on the mean quantum yield of hydrogen formation Q_{H_2}, as a function of substrate pressure, P_0, for runs of 30 to 60 minutes duration are given in Table II and Fig. 1.

The dependence of the mean quantum yield of hydrogen formation on exposure time is shown for three substrate pressures in Table III.

The values of $Q_{H_2}^0$, i.e., Q_{H_2} at zero time, given in Table III, were obtained by linear extrapolation on a semilog plot of the 10-, 4-, and 2-min values. It is seen from Table III that the primary quantum yield of hydrogen formation $Q_{H_2}^0$ is independent of cyclohexane pressure in the complete quenching region, at a mean value of 0.55 mole/einstein.

TABLE III. Mean quantum yield of hydrogen formation as a function of exposure time at three substrate pressures.

P_0 mm	Duration of run minutes	Q_{H_2} mole/einstein
...	0	0.50
27.9	2	0.46
28.1	4	0.43
27.9	10	0.36
28.0	60	0.29
28.5	60	0.29
...	0	0.56
51.5	2	0.54
52.3	4	0.50
52.8	10	0.43
51.6	60	0.36
...	0	0.58
73.5	2	0.58
72.0	4	0.54
74.6	4	0.54
72.4	10	0.50
72.7	10	0.48
69.0	30	0.40
70.6	60	0.39

In some of the 60-min runs, small particles of a translucent, wax-like solid were found intermingled with the droplets of liquid, indicating, presumably, a decomposition of the liquid product.

The mass spectra of the liquid nitrogen condensates showed unequivocally the presence of two condensable products, cyclohexene and bicyclohexyl. Cleavage of the cyclohexane ring would be expected to lead to the formation of *n*-hexane, dodecanes, *n*-hexylcyclohexane, and perhaps products with carbon numbers lower than six. The foregoing products were specifically sought for, and found absent. Hence it would seem reasonable to conclude that the cyclohexane ring remains stable during reaction.

In order to gain additional information on the heavy products of the reaction, larger quantities of material were prepared on the auxiliary system. Under these conditions some photolysis of the bicyclohexyl could occur. Two series of runs were performed, and in each case the heavy product was isolated by removal of the C-6 fraction by distillation. In Table IV, the physical properties of the heavy product are compared with those of pure bicyclohexyl.

TABLE IV. Physical properties of heavy product from two series of runs on the auxiliary system.

	Mol. wt.	C (Wt. %)	H (Wt. %)	n_D^{20}	Density (20°C)
Condensable product:					
A-4	184	...	...	1.4881	0.900
A-5	...	86.69	13.25	1.4846	0.902
Bicyclohexyl					
Theor.	166.3	86.66	13.34	...	...
Lit.[a]	...	...	...	1.4796	0.8846

[a] G. Egloff, *Physical Constants of Hydrocarbons* (Reinhold Publishing Corporation, New York, 1940), Vol. II.

From Table IV, it is apparent that hydrocarbons with carbon numbers greater than 12 are present. Recombination of radicals formed by the removal of a hydrogen atom from bicyclohexyl, either by photolysis or radical abstraction reactions, would result in the formation of quater-cyclohexyls, i.e., $C_{24}H_{42}$. Unfortunately, none of the quater-cyclohexyls has been prepared.

The mass spectra of the accumulated heavy product were found to correspond precisely to that for bicyclohexyl. Hence we may conclude that no other C-12 product than bicyclohexyl is present. Any C-24 compounds present in the heavy fraction would, of course, be too involatile for ordinary mass spectrometric detection. In order to circumvent this difficulty, a sample of the heavy product (A-4 series) was run on a Consolidated Engineering Corporation Mass Spectrometer with a special heated inlet system. The results of the analysis, using the "parent peak" method,[8] may be summarized as follows:

[8] M. J. O'Neal and T. P. Wier, Anal. Chem. **23**, 830 (1951).

(1) The predominant molecular type is a C-12 bicycloalkyl, i.e., bicyclohexyl. This compound formed *ca* 80 mole percent of the mixture.

(2) All the compounds present have two to four rings.

(3) The following types of compounds are absent: (a) normal paraffins. (b) Isoparaffins. (c) Monocyclo paraffins. (d) Mono olefins.

In Fig. 2, the infrared absorption spectra of pure bicyclohexyl and heavy product from the A-5 series are compared. The spectra are essentially the same, apart from the absorption peak present at 13.83 mμ in the product but absent in bicyclohexyl. Consequently the solid product present must be structurally very similar to bicyclohexyl.

From the above analytical data, as well as the kinetic data, it is assumed here that the solid products are quater-cyclohexyls.

From the mass spectra of the condensable products from each run, information on the dependence of the mean quantum yield of cyclohexene formation, Q_u, on substrate pressure and exposure time was obtained. The results are summarized in Table V (see Fig. 1). Since cyclohexene is only a very minor constituent of the condensed mixture of undecomposed substrate and products, the quantum yield data could be in error as much as 20 percent. Extrapolation of these data on a semilog plot led to a value of 0.17 ± 0.02 for the primary quantum yield of cyclohexene formation, independent of substrate pressure.

Since the only products of the cyclohexane reaction would seem to be cyclohexene, hydrogen, and bicyclohexyl, the stoichiometry of the reaction can be represented by the two equations

$$\text{Cyclo } C_6H_{12}=\text{Cyclo } C_6H_{10}+H_2,$$
$$\text{Cyclo } C_6H_{12}=\tfrac{1}{2}C_{12}H_{22}+\tfrac{1}{2}H_2.$$

Hence, the rate of bicyclohexyl formation and the rate of cyclohexane consumption can be calculated from the data on the hydrogen and cyclohexene rates.

Direct determination of the rates of bicyclohexyl formation from the mass spectral data gave somewhat lower values than those calculated from the stoichiometry. The reason for the discrepancy became apparent in experiments with synthetic mixtures of cyclohexane, cyclohexene, and bicyclohexyl. The low volatility of the bicyclohexyl prevented its quantitative recovery by liquid nitrogen condensation in the small freezeout trap attached to the reaction cell. Attempts to desorb the bicyclohexyl from the walls by warming the reaction cell increased the amount recovered, but the results were still 10 to 20 percent short of quantitative. Similar difficulties were encountered in the mass spectrometer.

From the stoichiometry of the reaction, taken in conjunction with the fact that the pressure decrease arises essentially from the condensation of the bicyclohexyl from the gas phase, the following relations among

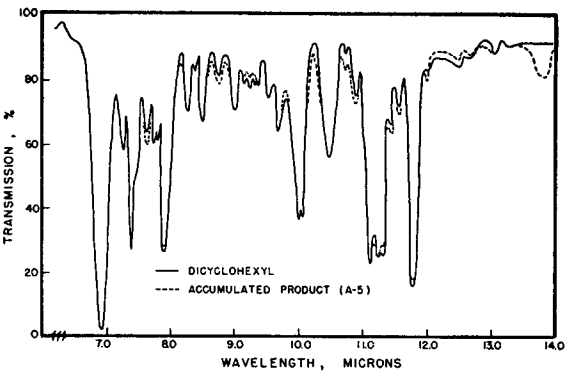

FIG. 2. Infrared absorption spectrum of dicyclohexyl and accumulated product.

the quantum yield should exist:

$$Q_C{}^P=Q_P+Q_{H_2}+Q_u,$$
$$Q_C=2Q_{H_2}-Q_u,$$
$$Q_{C_2}=Q_{H_2}-Q_u.$$

The meanings of the symbols are given in Table VI. In Fig. 1, the experimental quantities, Q_P (curve A), Q_{H_2} (curve B), and Q_u (curve C) are represented as functions of substrate pressure. From the best curves through the experimental points, interpolated values for decadic multiples of the pressure have been obtained and recorded in Table VI.

It is quite apparent from Table VI that the values of $Q_C{}^P$ and Q_C diverge rapidly with increasing substrate pressure. Experiments with liquid bicyclohexyl in the presence of cyclohexane vapor showed very clearly that the discrepancies in the values of the quantum yields of cyclohexane consumption calculated by the two methods were due almost exclusively to the solubility of cyclohexane in the bicyclohexyl formed during reaction.

In the next-to-the-last column of Table VI, the ideal solubilities of cyclohexane in Q_{C_2} moles of bicyclohexyl

TABLE V. Mean quantum yield of cyclohexene formation.

Initial cyclohexane pressure mm	Duration of run min	Mean quantum yield
31.0	30	0.012
40.2	30	0.012
51.5	2	0.11
52.23	4	0.092
52.0	15	0.028
51.6	60	0.008
69.0	30	0.024
70.6	60	0.008
72.4	10	0.052
73.6	2	0.123
74.1	30	0.016
79.2	60	0.004
80.0	15	0.044
81.5	5	0.092
85.2	60	0.012
87.8	30	0.048
91.2	60	0.016
93.3	50	0.040

TABLE VI. Quantum yield data for 30-min runs.[a]

P_0 mm	Q_P	Q_{H_2}	Q_u	Q_{C_2}	$Q_C{}^P$	Q_C	$Q_C{}^P-Q_C$	S moles	$(Q_C{}^P-Q_C)/S$
0	0	0	0	0	0	0	0	0	···
10	0.16	0.21	0	0.21	0.37	0.42	[−0.05]	0.02	···
20	0.26	0.27	0.005	0.26	0.53	0.53	0	0.05	···
30	0.33	0.31	0.010	0.30	0.65	0.61	0.04	0.10	0.4
40	0.39	0.33	0.010	0.32	0.73	0.65	0.08	0.17	0.5
50	0.46	0.35	0.015	0.33	0.82	0.69	0.13	0.23	0.6
60	0.55	0.37	0.020	0.35	0.94	0.72	0.22	0.35	0.6
70	0.67	0.39	0.020	0.37	1.08	0.76	0.32	0.52	0.6
80	0.82	0.41	0.025	0.39	1.26	0.80	0.46	0.78	0.6
90	1.02	0.43	0.030	0.40	1.48	0.83	0.65	1.20	0.5

[a] Explanation of symbols:

P_0 = Initial pressure of cyclohexane.
Q_P = Quantum yield of pressure decrease.
Q_{H_2} = Quantum yield of hydrogen formation.
Q_u = Quantum yield of cyclohexene formation.
Q_{C_2} = Quantum yield of bicyclohexyl formation $=Q_{H_2}-Q_u$.
$Q_C{}^P$ = Quantum yield of cyclohexane consumption from rate of pressure decrease $=Q_P+Q_{H_2}+Q_u$.
Q_C = Quantum yield of cyclohexane consumption from stoichiometry $=2Q_{H_2}-Q_u$.
S = Ideal solubility of cyclohexane in Q_{C_2} moles of bicyclohexyl.

are given for each pressure. In the last column of the table it is seen that $Q_C{}^P-Q_C$ only amounts to about 50–60 percent of the quantity of cyclohexane which could be taken up by the bicyclohexyl at equilibrium.

DISCUSSION

Before proposing a mechanism, the salient features of this investigation of the mercury-6($^3P_1$)-photosensitized decomposition of cyclohexane will be summarized.

(a) The reaction is pressure-decreasing, with the pressure decrease arising from the condensation of heavy product.

(b) The products of the cyclohexane reaction are hydrogen, bicyclohexyl, and cyclohexene. Upon prolonged irradiation, secondary reactions occur which result in the formation of high molecular weight material. From physical, mass spectral, and infrared data on the heavy product, it is concluded that the high molecular weight material is probably a mixture of quater-cyclohexyls, $C_{24}H_{42}$.

(c) Using a light intensity of 2.5×10^{-6} einstein/min, it was found that no appreciable secondary decomposition took place during 30-min exposures.

(d) In the 30-min runs, it was found that the mean quantum yields of cyclohexane disappearance, cyclohexene formation, and hydrogen formation increased slowly with increasing substrate pressure in the complete quenching region. At 90-mm cyclohexane pressure, the aforementioned mean quantum yields were found to be 0.83, 0.03, and 0.40, respectively.

(e) The mean quantum yield of hydrogen formation Q_{H_2} at constant substrate pressure was found to rise rapidly with decreasing exposure time. Extrapolation of Q_{H_2} to zero time, at three different substrate pressures, led to the value 0.55 for the initial quantum yield of hydrogen formation. A similar treatment of the cyclohexene data gave 0.17 for the initial quantum yield of cyclohexene formation.

(f) No mass spectral evidence was found for the presence of hexane, dodecanes, *n*-hexylcyclohexane, or products of carbon number less than 6. From this fact it is concluded that the cyclohexane ring remains stable during decomposition.

From the nature of the products, a mechanism similar to that which has been well established in the mercury-photosensitized reactions of the paraffins immediately suggests itself.

Under initial conditions, the following sequence is proposed:

$$C+\text{Hg } 6(^3P_1)\rightarrow R+\text{H}+\text{Hg } 6(^1S_0), \tag{1}$$

$$\text{H}+C\rightarrow \text{H}_2+R, \tag{2}$$

$$2R\rightarrow U+C, \tag{3}$$

$$2R\rightarrow C_2, \tag{4}$$

where C represents cyclohexane; R, cyclohexyl radical; U, cyclohexene; and C_2, bicyclohexyl. The assumption of the steady state for (H) and (R) leads to the following primary quantum yield relations:

$$Q_C{}^0=K\left[\frac{1+2r}{1+r}\right], \tag{5}$$

$$Q_{H_2}{}^0=K, \tag{6}$$

$$Q_u{}^0=K\left[\frac{1}{1+r}\right], \tag{7}$$

where $r=k_4/k_3$, the ratio of the rates of recombination to disproportionation for cyclohexyl radicals. The constant K is assumed to represent the fraction of quenching which leads to reaction. The fraction $1-K$ may well represent quenching to the metastable Hg-6($^3P_0$) state.

Since from Table III, $Q_{H_2}{}^0=0.55$, Eq. (6) gives $K=0.55$. Using $K=0.55$, and $Q_u{}^0=0.17$, we obtain from Eq. (7)

$$r=k_4/k_3=2.2.$$

Hence the proposed mechanism predicts that cyclohexyl

radicals recombine a little over twice as fast as they disproportionate.

From Eq. (5), the primary quantum yield of cyclohexane can be calculated:

$$Q_C^0 = (0.55)\left[\frac{1+2(2.2)}{1+2.2}\right] = 0.93.$$

From Table VI it can be seen that Q_C has attained the value 0.83 at 90 mm. The mechanism predicts that $Q_C \rightarrow Q_C^0$ with increasing substrate pressure.

From the sharp decline in Q_{H_2} and Q_u with increasing exposure time, it is assumed that under these conditions the cyclohexene rapidly reaches a steady-state concentration by the step

$$H + U \rightarrow R. \tag{8}$$

The sequence (1), (2), (3), (4), and (8) would, therefore, describe the reaction in the 30-min runs. The five-step mechanism yields the following relations:

$$Q_C^S = K\left[\frac{2r}{1+r}\right], \tag{9}$$

$$Q_{H_2}^S = K\left[\frac{r}{1+r}\right], \tag{10}$$

where the superscript indicates the instantaneous quantum yields when the cyclohexene has reached its steady-state concentration. Substituting the numerical values for K and r in (9) and (10), we obtain

$$Q_C^S = 0.76,$$
$$Q_{H_2}^S = 0.38.$$

The mean values of the quantum yields should fall between the initial and steady-state values. Since the onset of the complete quenching region begins at a substrate pressure of approximately 30 mm, the values of Q_C and Q_{H_2} at this pressure should lie, respectively, in the ranges 0.76–0.93, and 0.38–0.55. From Table VI, at 30 mm, $Q_C = 0.61$ and $Q_{H_2} = 0.31$; both somewhat lower than the values allowed by the mechanism. It is not felt, however, that this discrepancy represents an inadequacy in the proposed mechanism, but rather that it reflects errors in the extrapolation of the quantum yields to initial conditions.

CONCLUSIONS

From this investigation it would appear reasonable to conclude that cyclohexyl radicals are remarkably stable, showing little tendency either to isomerize or become hydrogenated. Their reactions seem to be limited to recombination and disproportionation. No evidence was found for atomic cracking reactions, and in this respect they differ from paraffinic free radicals.

In a publication shortly to be submitted to this journal, new data on the cyclopentane reaction will be presented and, in addition, our earlier work on cyclopentane and methylcyclopentane[2] will be reevaluated in the light of our present findings.

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