# Use of the Kinetic Isotope Effect as a Test for Homogeneous Unimolecular Gas Phase Reactions in Thermolytic Processes

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*Received July 27, 1975*

Experiments are described employing the kinetic isotope effect to discriminate between homogeneous and heterogeneous surface catalyzed reactions. Advantage is taken of the differences in isotope effect expected between the nonequilibrium statistical weight isotope effect (NESWIE) observed at low pressures and the conventional isotope effect observed at higher pressures for molecules containing up to approximately 15 atoms. No change in isotope effect as a function of pressure is expected for surface-catalyzed processes. The $k_H/k_D$ ratio for the thermal decomposition of diketene to ketene in a flow system is reported. At low pressures a value of $k_H/k_D$ of 0.91 was obtained while at pressures of 140 mm, $k_H/k_D$ was found to be 1.04 at 420 °C.

Interest in the study of thermolytic gas phase reactions has increased dramatically in the past decade.[1-4] This renaissance has been prompted to a large part by recent advances in theory[2,3] and technology of thermolytic processes.[4] One of the inherent difficulties in studying many thermolytic reactions in the gas phase at constant volume is the variety of secondary reactions which may follow the primary process. This complexity is often overcome by reducing the residence time of the reactants and products in the furnace by using flow methods. This has proven quite successful for the synthesis of many interesting and reactive molecules.[4] Flow methods, however, have not been extensively used by organic chemists to obtain mechanistic information. This can be attributed in part to a variety of obstacles associated with obtaining quantitative kinetic data.[5]

Surface effects in the pyrolysis of organic molecules in the gas phase are often not well understood. Their role may range from a means of energizing molecules to catalyzing specific processes which may or may not also occur homogeneously. Although several methods are routinely used to test for surface effects in static systems, these methods are generally not applicable to flow systems.[6] In flow systems, thermal activation by the surface can become the primary process of activating molecules, particularly in flash vacuum thermolysis. Differentiation between thermal activation and catalysis by the surface is thus further obscured. Mechanistic deductions from flash vacuum thermolysis, such as orbital symmetry considerations, do not require quantitative kinetic data. They do require the demonstration of unimolecularity.[7] Competitive kinetic isotope measurements to be described below afford a means of testing for the unimolecularity of a reaction, when run in a flow system.

One of the best tests for a homogeneous gas phase reaction is the falloff of the unimolecular rate constant, $k_{\text{uni}}$, with decreasing pressure [M].[8] At sufficiently low pressures, $k_2 > k_{-1}[M]$, the rate-determining step in the reaction of small molecules can become energization of the molecule (a molecule, A*, with sufficient internal energy to react, but randomly localized among the available quantum states, e.g., rotation, vibration). The efficiency of energization under these conditions is dependent upon the density of quantum states available. Isotopic substitution, specifically by deuterium, leads to an increase in the density of vibrational levels available. This results from the lower fundamental vibrational frequencies of R–D as compared to the R–H bond. Under conditions of low pressure an inverse isotope effect can result ($k_H/k_D < 1$). The magnitude of this effect depends upon the number of isotopic substitutions and can be much larger than conventional isotope effects measured at higher pressures. Furthermore, this effect is roughly independent of the position of isotopic substitution in the molecule. This inverse isotope effect has been observed in a number of constant volume experiments and has been termed a nonequilibrium statistical weight isotope effect (NESWIE).[8,28]

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} A^{\ddagger} \rightarrow \text{products}$$

$$k_{\text{uni}} = \frac{k_2 k_1[M]}{k_{-1}[M] + k_2}$$

M = any collision partner (e.g., the wall, A, or carrier gas)

The pressure dependence of the kinetic isotope effect can be used to discriminate between a homogeneous and heterogeneous process in the following way. In a competition experiment between appropriately deuterated and undeuterated reactant, relative reaction rates can be determined by the $k_H/k_D$ ratios. This ratio, regardless of the value, should remain invariant to the pressure of a carrier gas for a heterogeneous process, but would be expected to vary for a homogeneous process. This obtains because activation and catalysis of a heterogeneous process can occur simultaneously on the surface whereas the rate-determining step in a homogeneous process can be changed from energization of the molecule at low pressure (possibly on the surface) to collapse of the activated complex at higher carrier gas pressures. The converse of this is not necessarily true. Invariance of the kinetic isotope effect as a function of pressure is not a sufficient condition for a heterogeneous process.[9]

An interesting situation arises in the case where an observed chemical transformation involves a series of consecutive reactions. In this instance it is possible to have sequential homogeneous and heterogeneous processes. If the intermediate(s) in the transformation are thermodynamically accessible, the short contact times involved enhance the probability that they will be trapped. Otherwise, the information conveyed by the pressure dependence of the kinetic isotope effect relates only to the rate-determining step in the series. As an example of the limiting case of a multistep reaction, consider a reaction involving an intermediate which experiences small but comparable barriers for return to reactant and conversion to products.[10] In this instance the reaction would be expected to exhibit a pressure-dependent kinetic isotope effect respective only of the process (homogeneous or heterogeneous) which led to its formation. This conclusion is based on the condition that the intermediate, once formed, is energized with respect to all the barriers along the reaction coordinate and hence does not require additional collision induced energization.[17]

The thermolysis of diketene was chosen to demonstrate how

Table I. Low-Pressure Kinetic Isotope Effect for Diketene Thermolysis[a]

| Run no. | Temp, °C | Diketene[c] vapor pressure, mm | No. of passes[d] | Fraction reacted ($f$) | $R_{\mathrm{Dk}^0}$ | $R_{\mathrm{Dk}^f}$ | $R_{\mathrm{K}^f}$ | $F_{\mathrm{Dk}^\mathrm{D}}$ | $F_{\mathrm{Dk}^H}$ | $k_\mathrm{H}/k_\mathrm{D}$ (from ketene)[b] | $k_\mathrm{H}/k_\mathrm{D}$ (from diketene)[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 510 | 1.6 | 5 | 0.787 | 1.03 | 1.246 |  | 0.806 | 0.770 |  | 0.88 (0.88) |
| 2 | 510 | 1 | 5 | 0.61 | 1.05 | 1.18 |  | 0.631 | 0.592 |  | 0.88 (0.88) |
| 3 | 510 | 1 | 1 | 0.125 | 1.05 |  | 0.944 | 0.132 | 0.119 | 0.89 (0.89) |  |
| 4 | 510 | 8 | 1 | 0.084 | 1.05 |  | 0.923 | 0.0896 | 0.0786 | 0.87 (0.87) |  |
| 5 | 478 | 8 | 1 | 0.04 | 1.05 |  | 0.960 | 0.0210 | 0.0192 | 0.91 (0.91) |  |
| 6 | 420 | 1 | 1 | 0.0358 | 1.05 |  | 0.970 | 0.0372 | 0.0345 | 0.92 (0.92) |  |
| 7 | 410 | 1.6 | 2 | 0.018 | 1.05 |  | 0.954 | 0.0191 | 0.0174 | 0.91 (0.91) |  |

[a] For definitions of the symbols used in these tables and a description of Experimental conditons, see Experimental Section. [b] Estimated error ±0.03; isotope effects in parentheses are values calculated for reactions run at constant volume.[23] [c] Vapor pressures obtained by immersing samples in baths of appropriate temperature.[25] [d] Approximate residence time in oven, ~0.1 s/pass.

Table II. High-Pressure Kinetic Isotope Effect for Diketene Thermolysis[a]

| Run no. | Temp, °C | Diketene[c] vapor pressure, mm | Carrier[d] gas, mm | Fraction reacted ($f$) | $R_{\mathrm{Dk}^0}$ | $R_{\mathrm{Dk}^t}$ | $R_{\mathrm{K}^t}$ | $F_{\mathrm{Dk}^\mathrm{D}}$ | $F_{\mathrm{Dk}^\mathrm{H}}$ | $k_\mathrm{H}/k_\mathrm{D}$ (from ketene)[b] | $k_\mathrm{H}/k_\mathrm{D}$ (from diketene)[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 420 | 8 | $N_2$, 295 | 0.929 | 1.026 | 0.888 |  | 0.914 | 0.925 |  | 1.06 (1.06) |
| 9 | 420 | 8 | $N_2$, 140 | 0.852 | 1.026 | 0.931 |  | 0.860 | 0.873 |  | 1.06 (1.06) |
| 10 | 420 | 8 | $N_2$, 137 | 0.919 | 1.026 | 0.931 |  | 0.916 | 0.923 |  | 1.04 (1.04) |
| 11 | 345 | 8 | $N_2$, 146 | 0.224 | 1.026 |  | 1.075 | 0.219 | 0.229 | 1.06 (1.05) |  |
| 12 | 520 | 8 | $N_2$, 100 | 0.858 | 1.067 | 1.016 |  | 0.854 | 0.861 |  | 1.03 (1.03) |
| 13 | 520 | 8 | $N_2$, 72 | 0.844 | 1.067 | 1.005 |  | 0.839 | 0.849 |  | 1.04 (1.03) |
| 14 | 420 | 8 | Ar, 140 | 0.741 | 1.067 | 1.026 |  | 0.736 | 0.746 |  | 1.03 (1.03) |
| 15 | 420 | 8 | He, 140 | 0.852 | 1.020 | 0.949 |  | 0.846 | 0.857 |  | 1.05 (1.04) |
| 16[e] | 420 | 8 | $N_2$, 141 | 0.68 |  |  |  |  |  |  |  |
| 17[e] | 420 | 1.6 | $N_2$, 138 | 0.63 |  |  |  |  |  |  |  |

[a-c] See Table I. [d] Flow rates varied from 0.24 to 0.5 ml/s giving rise to calculated contact times of 1–8 s. [e] Flow rate 0.5 ml/s.

the pressure dependence of the kinetic isotope effect could be used to test for a homogeneous reaction. This substrate was selected for a variety of reasons. Earlier work of Rice and Greenburg cast some doubt as to whether the dimerization of ketene could occur homogeneously in the gas phase.[18] Furthermore despite the industrial importance of diketene, relatively little concerning the mechanism of its formation has appeared in the literature.[19,20] Finally, as is typical of many other organic reactions, diketene is converted to a variety of products in a static system;[21] a quantitative conversion to ketene occurs in a flow system at 500 °C.[19]

## Experimental Section

The thermolysis of diketene was performed in a 1-cm diameter quartz tube at temperatures between 410 and 520 °C with and without a carrier gas. Prior to each experiment the vacuum of the system was reduced to approximately 1 μm. In order to obtain reasonable conversion to products in the absence of carrier gas, it was necessary at some temperatures to recycle the reactant. The temperatures reported in Tables I and II were controlled to ±15 °C. The carrier gas was passed through a liquid nitrogen trap before use. In a typical experiment approximately 50 mg of a mixture consisting of equal molar amounts of diketene and perdeuteriodiketene were thermolyzed. Ketene and diketene were trapped at liquid nitrogen temperatures, separated at dry ice–acetone temperatures, and analyzed. The isotopic ratios were measured on an AEI MS 12 mass spectrometer at 70 eV by analyzing the parent ion of the reactants at high conversion and mass analysis of the products at low conversion. Analysis of dideuterioketene was complicated by traces of carbon dioxide. Consequently, the ketene mixture was allowed to react with a threefold excess of methanol prior to analysis and thus analyzed as methyl acetate.

**Calculations.** The isotope effects were calculated from the following equation derived by Benton for flow systems conducted at constant pressure assuming plug flow and negligible diffusion.[22]

$$k_\mathrm{H}/k_\mathrm{D} = \frac{2\left[\ln\dfrac{1}{1 - F_{\mathrm{Dk}^\mathrm{H}}}\right] - F_{\mathrm{Dk}^\mathrm{H}}}{2\left[\ln\dfrac{1}{1 - F_{\mathrm{Dk}^\mathrm{D}}}\right] - F_{\mathrm{Dk}^\mathrm{D}}}$$

The term $F_\mathrm{Dk}$ refers to the fraction of reacted diketene at time $t$ and the superscripts refer to deuterated and undeuterated species and are included in Tables I and II. For comparison, the isotope effects calculated for reactions occurring at constant volume are also included in Tables I and II in parentheses. The following equations were used.[23] For isotopic analysis of residual diketene (DK)

$$k_\mathrm{H}/k_\mathrm{D} - 1 = \frac{\log A}{\log\,[(1 - f)B]}$$

$$\text{where } A = R_{\mathrm{Dk}^t}/R_{\mathrm{Dk}^0};\ B = \frac{1 + R_{\mathrm{Dk}^0}}{1 + R_{\mathrm{Dk}^t}};\ 1 - f_\mathrm{Dk} = \frac{[\mathrm{Dk}^t{}_\mathrm{H}] + [\mathrm{Dk}^t{}_\mathrm{D}]}{[\mathrm{Dk}^0{}_\mathrm{H}] + [\mathrm{Dk}^0{}_\mathrm{D}]}$$

and for initially formed ketene (K)

$$k_\mathrm{H}/k_\mathrm{D} - 1 = \frac{\log\left[1 + C\left(\dfrac{D}{1 - D}\right)\right]}{\log\,[1 - D]}$$

$$\text{where } C = \frac{R_{\mathrm{Dk}^0} - R_{\mathrm{K}^t}}{R_{\mathrm{Dk}^0}};\ D = f_\mathrm{K}\left[\frac{1 + R_{\mathrm{Dk}^0}}{1 + R_{\mathrm{K}^t}}\right];$$

$$f_\mathrm{K} = \frac{[\mathrm{K}^t{}_\mathrm{D}]}{2[\mathrm{Dk}^0{}_\mathrm{D}]}\,\frac{(1 + R_{\mathrm{k}^t})}{(1 + R_{\mathrm{Dk}^0})}$$

The terms used in these two equations, $R_{\mathrm{Dk}^0}$, $R_{\mathrm{Dk}^t}$, $R_{\mathrm{K}^t}$, $f$, refer to the initial ratios of diketene to perdeuteriodiketene, diketene to perdeuteriodiketene at time $t$, ketene to dideuterioketene at time $t$, and the fraction of reaction at time $t$ as defined, respectively.

**Ketene and Diketene.** Ketene and dideuterioketene were prepared from the corresponding anhydrides (Aldrich Chemical Co., Milwaukee, Wis.) by thermolysis in an evacuated hot tube at 500 °C. The acetic acid was trapped at dry ice–acetone temperatures and the ketene was trapped in liquid nitrogen. The isotopic purity of dideuterioketene exceeded 99% as analyzed by mass spectroscopy. Diketene was prepared by allowing a sealed tube of ketene to stand at −10 °C overnight. The diketene was isolated by bulb to bulb distillation on a vacuum line. NMR analysis suggested a purity in excess of 95%. Upon pyrolysis, better than 95% of the theoretical amount of ketene could be recovered.

## Results

The experimental results for the thermolysis of diketene are shown in Tables I and II. Table I lists the results of experiments performed under a variety of experimental conditions in the absence of carrier gas while the results obtained with carrier gas are reproduced in Table II. In both cases the isotope effects calculated were not sensitive to whether the equations for constant volume (static system) or constant pressure (flow) were used. Entries 16 and 17 in Table II were performed with unlabeled diketene and are included to demonstrate that the thermolysis of diketene is first order and is consistent with earlier reports.[19] Thermolysis of diketene at different concentrations but otherwise similar conditions of flow and pressure gave, within experimental error, the same fractional conversion. The fraction of reaction would be expected to increase for a zero-order reaction and to decrease for second or higher order reactions as the concentration of diketene decreased. The isotope effects measured at both high and low pressures do not seem particularly sensitive to temperature and hence it can be concluded that the changes in the kinetic isotope effect reflected in Tables I and II are not due to the failure of diketene to achieve thermal equilibrium when passed through without a carrier gas. It is believed that the isotope effect measured at high pressure is real (>1) but it is not presently known how it would compare to the isotope effect measured at the same temperature in a constant volume experiment. Comparison of runs 8 and 9 in Table II suggests that the high-pressure region has been reached at 140 mm pressure. Runs 10, 14, and 15 demonstrate the invariance of $k_H/k_D$ to carrier gas. Finally, the isotope effect observed at low pressure can be contrasted to that observed under similar conditions at higher pressure. These results clearly indicate a pressure dependence on the observed isotope effect.[27]

The normal secondary deuterium isotope effect ($k_H/k_D > 1$) measured at high pressures is consistent with the results expected for a carbon atom undergoing an sp$^3$ → sp$^2$ interconversion during the rate-determining step. This suggests that carbon–carbon bond breaking is involved during the slow step of diketene thermolysis. The low-pressure inverse isotope effect is exactly what is expected on the basis of the NESWIE.[26]

Advantages of this method of testing for homogeneous reactions include the fact the the experimental apparatus is easy to construct, precise temperature control is not essential, and flow rates need not be accurately reproducible. Although quartz tubes were used in these experiments, there are no limitations to the type of material that can be used. Furthermore, the magnitude of the NESWIE effect is dependent primarily on the number of isotopic substitutions, and not necessarily on how close they are to the reaction site. Thus deuterium substitution remote from the reaction site would be expected to give a NESWIE effect at low pressures and a $k_H/k_D = 1$ at higher pressures.[8]

The major limitation to this method of ascertaining the homogeneous character of a reaction is that the falloff region is not always experimentally accessible. The largest molecule whose falloff region has been experimentally investigated has contained approximately 15 atoms.[8,24] Furthermore, the pressures at which the falloff is accessable decreases rapidly with increasing molecule size.[8,26] However, this method may be applicable to slightly larger molecules since it is not necessary to obtain the limiting low-pressure NESWIE to apply this method. All that is needed to demonstrate the NESWIE is a change in the limiting high-pressure value of $k_H/k_D$ at constant temperature as the pressure is decreased.

**Registry No.**—Ketene, 463-51-4; dideuterioketene, 4789-21-3; acetic anhydride, 108-24-7; diketene, 674-82-8.

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(10) A diradical has been suggested as such an intermediate. Consider a surface-catalyzed ring opening to give a singlet diradical which then diffuses off the surface. If the diradical is not energized with respect to product formation, a pressure-dependent kinetic isotope effect could be observed because the second step will show a pressure dependence typical of a homogeneous process, while the recombination reaction, which must be surface catalyzed (principle of microscopic reversibility), will not. Competition between these two processes as a function of pressure may lead to changes in isotopic discrimination. Activation energies for the recombination of two radicals are very small providing that there is no spin barrier.[11] Recent theoretical and experimental results suggests similar recombination barriers for diradicals. In some cases the barriers may be vanishingly small.[12] Catalysis by a surface becomes a moot point if the activation energies of the homogeneous reaction simply reflect the thermodynamic bond strengths involved. Nevertheless, should a reaction involve sequential heterogeneous and homogeneous steps as described above for the diradical, and small barrier separating intermediate from products relative to the total barrier separating reactant from product assures an operating temperature sufficiently high that the pressure at which the unimolecular rate constant for the homogeneous step begins to decline will be anomalously high.[13] Comparison of the falloff pressure (in this case the pressure region in which the KIE is variable) to that expected for the corresponding hypothetical homogeneous unimolecular process permits a distinction between the two possibilities. This conclusion is based on the experimental observation that for two competing reactions at low pressure, the reaction with the lower activation energy is furthest into the falloff region.[13,14] A theoretical relation between the change in falloff pressure and temperature is given by Slater's theory.[13,15]

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# Reactions of Hydroperoxy Radicals. Comparison of Reactivity with Organic Peroxy Radicals

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*Received March 11, 1976*

1,4-Cyclohexadiene, which oxidizes with the hydroperoxy radical as a chain carrier, has been cooxidized with butadiene, tetralin, and tetramethylethylene at 50 °C. The relative reactivities of 1,4-cyclohexadiene, butadiene, and tetralin toward the hydroperoxy radical are 1.0:0.23:0.18, while toward the butadiene and tetralin peroxy radicals they are 1.0:0.041:0.012 and 1.0:0.033:0.015, respectively. Thus the hydroperoxy radical is significantly less selective than the organic peroxy radicals generated from butadiene and tetralin. The cooxidation of 1,4-cyclohexadiene with tetramethylethylene indicates that the hydroperoxy radical has a greater tendency to form the tetramethylethylene epoxide than does the tetramethylethylene peroxy radical. This effect is due to a higher tendency of the hydroperoxy radical to add to the olefin to form the β-peroxyalkyl radical, although the rearrangement of this adduct to form the epoxide is somewhat slower than that of the β-alkylperoxyalkyl radical.

Earlier studies[1–3] have shown that cyclic olefins, conjugated olefins, and aralkanes generally have the same relative reactivity (±20%) toward the various corresponding peroxy radicals. For these peroxy radicals, the organic portions are sufficiently removed from the free valences so that they have little inductive or steric effect on reactivity. However, in one case where steric interference should be maximized,[2] the selectivities for the two peroxy radicals vary by a factor of 2 toward the same two hydrocarbons. This paper gives the reactivities of several hydrocarbons toward the hydroperoxy radical, the simplest of all peroxy radicals, and compares them with reactivities toward typical organic peroxy radicals.

We have shown that oxygen abstracts a hydrogen from the cyclohexadienyl radical in the main propagation step in the oxidation of 1,4-cyclohexadiene.[4] The propagation cycle is

$$HO_2\cdot + C_6H_8 \rightarrow H_2O_2 + C_6H_7\cdot \qquad (1)$$

$$C_6H_7\cdot + O_2 \rightarrow C_6H_6 + HO_2\cdot \qquad (2)$$

Thus cooxidation of 1,4-cyclohexadiene with a second hydrocarbon (RH) will involve the following propagation reactions:

$$HO_2\cdot + C_6H_8 \rightarrow H_2O_2 + C_6H_7\cdot \qquad (3)$$

$$HO_2\cdot + RH \rightarrow H_2O_2 + R\cdot \qquad (4)$$

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot \qquad (5)$$

$$RO_2\cdot + 1,4\text{-}C_6H_8 \rightarrow RO_2H + C_6H_7\cdot \qquad (6)$$

From the consumption of each reactant (measured by disappearance of reactant or formation of products), the two reactivity ratios, $r_{HO_2\cdot} = k_3/k_4$ and $r_{RO_2\cdot} = k_5/k_6$, are determined by using standard copolymerization and analysis techniques.[1] Thus if the two parent hydrocarbons have different relative reactivities toward each peroxy radical, then $r_{HO_2\cdot} \neq 1/r_{RO_2\cdot}$.

## Experimental Section

Reactions were carried out using vacuum line procedures. All hydrocarbons were purchased through common commercial channels. 1,4-Cyclohexadiene (>99.8%), tetralin (>99.8%), tetramethylethylene (98.4%), and chlorobenzene (>99.9%) were passed through silica gel, stored over calcium hydride, and distilled into the reaction vessel as needed. Butadiene (99.88%) was stored as a gas in the vacuum line after distillation from −78 °C, and was measured as a gas in a standard bulb of the vacuum line. Other compounds that were liquids at room temperature were measured as liquids in calibrated tubes in the vacuum line. All reactions were carried out in a water bath at 50 (±0.1) °C. Gas–liquid mixing maintained by a Burell wrist-action shaker (330 cycles/min) and a Vibro Mixer (7500 cycles/min) gave identical results. The analyses of $H_2O_2$ and $H_2O$ at the completion of the reaction were described previously.[4]

## Results

**Cooxidations of 1,4-Cyclohexadiene and 1,3-Butadiene.** Table I summarizes data for the cooxidation of 1,4-cyclohexadiene and 1,3-butadiene. The consumption of 1,4-cyclohexadiene was measured by formation of benzene, since reactions 3 and 6 are followed immediately by reaction 2. Less water (after reduction of $H_2O_2$) than benzene is formed because many of the hydroperoxy radicals add to butadiene. The amounts of hydrogen peroxide detected (not reported) are less than the water found after decomposition of hydrogen peroxide; therefore some decomposition

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (7)$$

occurs during the reaction as was observed previously.[4] The oxygen consumption is corrected for this decomposition by adding one-half the value of water present at the end of the reaction.

The consumption of butadiene is measured in four different ways. The first method is by measuring the difference in the butadiene before and after reaction; this entails separating butadiene from the reaction mixture, then measuring it as a gas in the standard bulb of the vacuum line. The efficiency of the separation was checked by GLC and correction made when necessary. The second procedure requires an assumption that 1 mol of oxygen is consumed for each mole of hydrocarbon consumed. Thus

$$\Delta 1,4\text{-}C_6H_8 + \Delta\text{hydrocarbon} = \Delta O_2\ (\text{corrected}) \qquad (8)$$

This equation is valid when chain lengths are long. Since we have measured the consumptions of oxygen (corrected) and 1,4-cyclohexadiene, the butadiene consumption is obtained