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# Deuterium Isotope Effects on Rates of Methylene Radical Insertion into C-H Bonds[1]

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A limited number of measurements of deuterium isotope effects on the rates of methylene insertion into C-H and C-D bonds have been made. Chesick[2] reported a ratio of $k_H/k_D = 1.3$ for secondary C-H and C-D bonds in propane. Simons and Rabinovitch[3] obtained ratios in the range 1.6-2.0 for insertion into the allylic and vinylic C-H bonds of butene-2 and butene-2-$d_8$. Most recently, Majer, Capey and Robb,[4] by the consideration of reactant peak height ratios before and after reaction, have obtained an inverse effect of 0.7 for insertion into the C-H and C-D bonds of cyclohexane and cyclohexane-$d_{12}$. The measurement of the change in isotopic composition of the reactants may not be accurate under the usual conditions, so ~~that~~ it seemed desirable to verify this unusual result by measurement of the proportions of products of insertion, i.e. of methyl cyclohexane~~$-d_6$~~ and * ~~-d~~12. The isotope effect for insertion into cyclopropane and cyclopropane-$d_6$ was also examined for comparison; D(C-H) is considerably stronger in this case.

meth. cyclohexane-d12.

## Experimental

Cyclohexane from Eastman Organic Chemicals was purified by gas chromatography. The cyclohexane-$d_{12}$ was obtained from Merck, Sharpe and Dohme of Canada. Mass spectral analysis showed that the main isotopic impurity was 7.6% cyclohexane-$d_{11}$; the correction to the final data for this contaminant amounted to 0.2%.

Gas chromatographic analysis showed that other impurities were present to the extent of < 0.4% and the compound was used without purification.

A cyclopropane —cyclopropane-$d_6$ mixture was obtained from Dr. A. T. Blades, whom we thank; the deutero-compound contained 7% of -$d_5$ impurity which entailed a correction to the calculations of only 0.35%.

The methylene source was diazomethane, photolyzed for up to 2 hr. in seasoned pyrex reaction vessels at 25° with the filtered radiation (4358 Å) of a G.E. AH-6 mercury lamp. Reactions were performed in or near the high-pressure region: at 7-10.5 cm for the cyclohexane system, and 170-220 cm for the cyclopropane system. By the "high pressure region" is meant a pressure sufficiently high so that virtually all of the chemically activated insertion products are collisionally deactivated rather than undergoing reaction. Mixtures of each pair of isotopic compounds were reacted with methylene.

The cyclohexane system was analyzed on a 300 ft. squalane capillary column and the cyclopropane system on a 60 ft. x 1/8 in. column of 15% dinonyl phthalate on Chromosorb-P. Analyses were made with a hydrogen flame ionization detector.

## Results

The treatment of the primary data for cyclopropane (Table I) involved a correction to the methyl cyclopropane products for decomposition. At the highest pressure used ~20% of decomposition of the methyl cyclopropanes occurred; the light methyl cyclopropane decomposed faster than the deuterated species, as expected.[3b]

Although the columns resolved the various light and $-d_6$ product peaks, only the 1-butene-$d_o$ and $-d_6$ and the cis-2-butene-$d_o$ and $-d_6$ peaks were free from overlap with other products and could be accurately measured. The amounts of trans-butene-2 and isobutene were assumed from the data of Butler and Kistiakowsky;[5] this is a satisfactory procedure since complete neglect of these products would affect the measured ratio by only 1-2%.

No such difficulties were encountered in the cyclohexane system; the solitary pair of methyl cyclohexane-$d_o$ and $-d_{12}$ products (Table II) was readily resolved completely.

The data were treated as follows. The percentage reaction was between 1 and 23%; a correction to the initial proportions of reactants was made so as to give the average ratio of the mixture during each run. The yield of products was then directly related to this average composition. Inaccuracy in the measurement of final reactant composition precludes the use of an exact analytical expression. The tables show that averaging is satisfactory.

The isotopic ratio, $k_H/k_D$, for methylene insertion into the carbon-hydrogen bonds of cyclopropane is 1.29; that for cyclohexane is 1.32. This result differs from that of Majer, et. al. These authors give a formulation of the kinetic equations (there is a typographical error in their paper) which is valid for a small amount of depletion of the reactants; their equations would be inappropriate in principle at large amounts of reaction such that reactant composition was appreciably altered. A more exact formulation will be found in ref. 6; it is not employed in the present paper for the reason mentioned above.

## Discussion

The present ratios are the same as Chesick's value of 1.3 for secondary bonds, despite a pronounced variation in C-H bond dissociation energies[7] of the species studied. These results differ from the values obtained[3] for the unsaturated pair, cis-butene-2-$d_0$ and -$d_8$. However the comparison is not a simple one, and the latter measurements involved still another comparison (with ethylene) of the relative rates of the competing processes of double bond addition. A check of the butene values was made here by direct internal comparison of a mixture of the two butenes. Such a check involved a fairly complex analytical separation of the various product and reactant species, and also of the isotopic pairs. The determination was most accurate for allylic insertion since the pentene-2 insertion product is favored statistically; an average ratio of 1.9 was found, in agreement with the earlier work.

The comparatively small isotopic values are not inconsistent with our earlier idea[3a] of the importance of C-H stretching as an aspect of the reaction coordinate. The isotopic ratio, $k_H k_D = 1.3$, cannot be simply related to the conventional predictions of absolute rate theory: first, the present systems are of non-equilibrium type with respect to the ambient temperature since the singlet methylene radicals are formed, on photolysis, with some excess vibrational energy[8] and excess translational energy as well;[9] also, the energy of the radicals has varied between the studies of various workers, who have used different methylene sources and photolysis wavelengths; furthermore, it is still not definite whether lower energy radicals are more discriminating (at least in the gas phase) in their insertion behavior;[3] finally, the addition and insertion reactions of these radicals involve an unknown collision efficiency, possibly unity in the former case, and unknown activation energies, probably close to zero.

## References

1. Supported by the Office of Naval Research.
2. J. P. Chesick, J. Am. Chem. Soc., **84**, 2448 (1962).
3. (a) J. W. Simons and B. S. Rabinovitch, J. Am. Chem. Soc., **85**, 1023 (1963);
   (b) *idem*, J. Phys. Chem., **68**, 1322 (1964).
4. J. R. Majer, W. D. Capey, and J. C. Robb, Nature, **203**, 294 (1964).
5. J. N. Butler and G. B. Kistiakowsky, J. Am. Chem. Soc., **82**, 759 (1960).
6. D. W. Placzek, Ph.D. thesis, University of Washington, 1965.
7. J. W. Root and F. S. Rowland, J. Phys. Chem., **68**, 1226 (1964).
8. D. W. Setser and B. S. Rabinovitch, Can. J. Chem., **40**, 1425 (1962).
9. H. M. Frey and G. B. Kistaikowsky, J. Am. Chem. Soc., **79**, 6373 (1957).

Table I: Reaction of Methylene with Cyclopropane Mixture[a] (25°)

| Total press. (cm) | 340 | | 380 | | 250 | |
|---|---|---|---|---|---|---|
| % reaction | 2.6% | | 2.0% | | 0.9% | |
| Product composition[b] | $C_3H_6$ | $C_3D_6$ | $C_3H_6$ | $C_3D_6$ | $C_3H_6$ | $C_3D_6$ |
| methyl cyclopropane | 175 | 35.3 | 222.7 | 45.0 | 333.1 | 67.0 |
| butene-1 | 21.6 | 3.3 | 26.0 | 3.3 | 22.9 | 3.3 |
| *cis*-butene-2 | 7.2 | 1.1 | 9.5 | 1.2 | 8.7 | 1.3 |
| *trans*-butene-2 | 7.2 | 1.1 | 9.5 | 1.2 | 8.7 | 1.3 |
| isobutene | 6.5 | 1.0 | 7.8 | 1.0 | 6.9 | 1.0 |
| total | 217.6 | 41.9 | 275.4 | 51.7 | 380.2 | 73.9 |
| $k_H/k_D$ | 1.29 | | 1.31 | | 1.27 | |

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a) Initial composition: $C_3H_6/C_3D_6 = 4.05$

b) Relative amounts of products in arbitrary units.

Table II: Reaction of Methylene with Cyclohexane Mixture[a]

| Total press. (cm) | 7 | 7 | 8 | 8 | 10.5 |
|---|---|---|---|---|---|
| % reaction | 22.5 | 19.6 | 19.2 | 19.0 | 6.34 |
| $C_6H_{12}/C_6D_{12}$ (aver.)[b] | 2.86 | 2.87 | 2.86 | 2.87 | 2.90 |
| $C_7H_{14}/C_7H_2D_{12}$ | 3.66 | 3.88 | 3.68 | 3.73 | 4.03 |
| $k_H/k_D$ | 1.28 | 1.36 | 1.29 | 1.30 | 1.39 |

a) Initial composition <u>cyclo</u>-$C_6H_{12}$/<u>cyclo</u>-$C_6D_{12}$ = 2.93

b) Average ratio of reactant mixture corrected for unequal depletion of light and heavy species.