

Acidity of Hydrocarbons. XXXI. Kinetic Acidities of Small-Ring Cycloalkanes and Correlation with $J(^{13}\text{C}-\text{H})^1$

Sir:

Although the stability of carbanions with localized charge is known to depend qualitatively on the amount of s character in the lone pair,² few quantitative correlations are available.³ We report here the kinetic acidities of the cycloalkanes from cyclopropane to cyclooctane as measured by cesium cyclohexylamide (CsCHA) catalyzed tritium incorporation from N-tritiated cyclohexylamine. Cyclopropane and cyclobutane were exchanged with benzene as a standard, and kinetic aliquots were measured by radio-gas chromatography.⁴ The other cycloalkanes were exchanged as mixtures with cyclohexane, as described previously for cyclopentane and cycloheptane.^{1b} The reactivities cover a range of 10^5 in rate and are summarized in Table I.

Table I. Kinetic Acidities of Hydrocarbons toward Cesium Cyclohexylamide at 50°

Hydrocarbon	Relative rate	$J(^{13}\text{C}-\text{H})$
Cyclopropane	$(7.0 \pm 0.9) \times 10^4$	161 ^a
Cyclobutane	28 ± 10	134 ^b
Cyclopentane	5.72 ± 0.27	128 ^{a,b}
Cyclohexane	1.00	123, ^a 124 ^b
Cycloheptane	0.76 ± 0.09	123 ^b
Cyclooctane	0.64 ± 0.06	122 ^b

^a N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959). ^b C. S. Foote, *Tetrahedron Letters*, 579 (1963).

Closs and Larrabee³ found previously a quantitative correlation of kinetic acidities of some bicyclobutane and cyclopropene derivatives with the appropriate $J(^{13}\text{C}-\text{H})$. For the cycloalkanes, such coupling constants, which appear to be valid measures of s character in hydrocarbons, are included in Table I; Figure 1 contains a plot of log relative rate against these coupling constants. The linear correlation obtained indicates that the dominant factor in cycloalkane acidity is the amount of s character in the exocyclic C-H bond.

A simple extrapolation gives a reactivity of 7×10^5 for $\text{C}_{\text{sp}^2}-\text{H}$ relative to cyclohexane, or 0.008 relative to benzene. Previously, we applied a simple field-effect function to the kinetic acidity of arene hydrogens toward lithium cyclohexylamide (LiCHA).⁵ An extrapolation of this correlation to zero field effect gives a reactivity of 0.025 relative to benzene for an isolated $\text{C}_{\text{sp}^2}-\text{H}$. Thus, two independent approaches give about the same value for the kinetic acidity of a trigonal C-H bond. This agreement also indicates

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(2) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 48.

(3) G. L. Closs and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965).

(4) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).

(5) A. Streitwieser, Jr., and R. G. Lawler, *ibid.*, **87**, 5388 (1965).

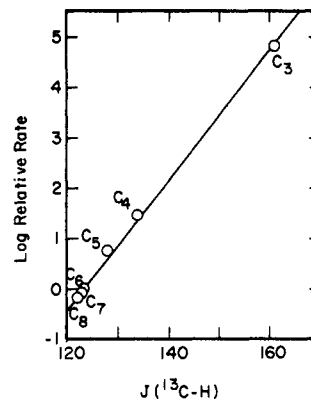


Figure 1. Correlation of tritium exchange rates with CsCHA of cycloalkanes compared to $J(^{13}\text{C}-\text{H})$. The least-squares line is $\log \text{relative rate} = (0.129 \pm 0.003)J(^{13}\text{C}-\text{H}) - 15.90 \pm 0.38$; standard deviation, 0.095; correlation coefficient, 0.999.

that both of these kinetic acidity measures are scaled similarly, *i.e.*, cycloalkanes with CsCHA and arenes with LiCHA have similar Brønsted coefficients.

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Acidity of Hydrocarbons. XXXII. Kinetic Acidities of Medium-Sized Cycloalkanes. Pyramidal Alkyl Anions¹

Sir:

We report here the kinetic acidities of medium-ring cycloalkanes from C_9 to C_{14} by the cesium cyclohexylamide (CsCHA) catalyzed tritioderprotonation method previously developed with cyclohexane² and other cycloalkanes. In this series internal strains from hydrogen oppositions vary substantially, but hybridization differences (as measured by $J(^{13}\text{C}-\text{H})$) are small (Table I).

The hydrocarbons were obtained commercially or synthesized in standard ways. Alkene impurities were removed by successive treatments with potassium permanganate and sulfuric acid and the final products were obtained by glpc or by sublimation. A mixture of hydrocarbons was treated kinetically with CsCHA in cyclohexylamine-N-*t* as described previously^{1b,3} to give directly the relative rates summarized in Table I.

Reactions involving carbonium ions and radicals generally show enhanced rates for the medium-ring cycloalkyls with peaks close to cyclodecane. Examples are the acetolyses of cycloalkyl tosylates^{3,4} and the

(1) (a) This research was supported in part by Grant GM-12855 of the National Institutes of Health, U. S. Public Health Service. (b) Paper XXXI: A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Am. Chem. Soc.*, **91**, 529 (1969).

(2) A. Streitwieser, Jr., W. R. Young, and R. A. Caldwell, *ibid.*, **91**, 527 (1969).

(3) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(4) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).