The Reactions of Monofluorocarbene with Olefins in the Gas Phase[1]

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Abstract: The chemical reactions of monofluorocarbene to form the corresponding fluorocyclopropanes have been studied with eight hydrocarbon olefins, utilizing the tritium-labeled carbene, CTF. The species CTF was formed by the unimolecular decomposition of excited CHTFX*, which was itself formed by energetic tritium atom reactions with polyhalomethanes, particularly CH_2F_2. The addition of CTF to the double bond of either *cis*- or *trans*-2-butene is >99% stereospecific and is not affected by small amounts of molecular oxygen. *syn* and *anti* isomers are formed in equal yield for propene and in each other case for which they exist. No insertion of CTF into the C–H bonds of olefins has been found. All of the observations are consistent with the reactions of CTF in a singlet electronic ground state. The absence of isomerization of excited fluorocyclopropane to the fluoropropenes indicates that ≤ 75 kcal/mole is released by CTF addition to ethylene, corresponding to an increased stabilization of ≥ 25 kcal/mole for F in CHF relative to H in CH_2. Relative efficiencies of reaction of CTF with olefins in direct competition vary by a factor of 6 between ethylene and tetramethylethylene. The temperature dependence of these relative rates indicates that the variation is almost entirely the result of differences in activation energy for monofluorocarbene addition to olefins. An isotope effect of 1.18 was found, favoring reaction with C_2H_4 over reaction with C_2D_4.

The substitution reactions of energetic tritium atoms from nuclear recoil into hydrocarbons and halocarbons, as in (1) and (2), have been shown to form

$$T^* + RH \longrightarrow RT^* + H \tag{1}$$

$$T^* + RX \longrightarrow RT^* + X \tag{2}$$

radioactive species, RT*, sufficiently excited that they are able to undergo decomposition or isomerization reactions on a time scale competitive with collisional deexcitation in both the gas phase and in condensed phases.[2-6] The substitution of T for H in cyclobutane has been shown to deposit excitation energies in the 3–7-ev range, leading to decomposition to C_2H_3T for 18 to 54% of the c-C_4H_7T molecules originally formed, depending upon the phase and pressure.[4] Similar decompositions have been demonstrated leading to CH_2T from CH_2TCl^*, C_2H_3T from C_2H_4TCl, and for the decomposition of several excited alkane-*t* molecules.[5-9]

While these decomposition and isomerization process have been previously known, for the most part, from photolytic or pyrolytic studies, the fact that recoil tritium substitution processes are usually accompanied by the deposition of large amounts of excitation energy provides a new approach to the study of the unimolecular decomposition of excited molecules.[10] A study of the radioactive products obtained from CH_2Cl_2 has demonstrated the presence of CTCl as a decomposition product through its reaction with ethylene to form cyclopropyl-*t* chloride;[11] similar studies with CH_2ClF and CH_2F_2 have indicated the formation of CTF, detected by its reaction with ethylene to form the corresponding cyclopropyl-*t* fluoride.[12] The basic sequence of reactions with CH_2F_2 is given by[13]

$$T^* + CH_2F_2 \longrightarrow CHTF_2^* + H \tag{3}$$

$$CHTF_2^* \longrightarrow CTF + HF \tag{4}$$

$$CTF + \text{olefin} \longrightarrow \text{fluorocyclopropane-}t \tag{5}$$

Our intention with the present series of experiments has been to investigate systematically the reactions of monofluorocarbene with olefins as a test of the potential of the recoil tritium excitation method. Simultaneously, we also have obtained information about the reactions of the heretofore unknown monofluorocarbene for comparison with the much better known reactions of carbene and dihalocarbene,[14,15] and the recently determined properties of monochlorocarbene.[16,17]

Experimental Section

General Procedure of Recoil Tritium Reactions. The basic characteristic of recoil tritium reactions is that the energetic tritium atoms are produced *in situ* in a gas bulb or in a capillary through the thermal neutron reaction $He^3(n,p)T$ or $Li^6(n,\alpha)T$. Extensive de-

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[1] This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126. This work was presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[2] J. K. Lee, B. Musgrave, and F. S. Rowland, *Can. J. Chem.*, **38**, 1756 (1960).

[3] E. K. C. Lee and F. S. Rowland, *J. Chem. Phys.*, **36**, 554 (1962).

[4] E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963).

[5] Y.-N. Tang, E. K. C. Lee, and F. S. Rowland, *ibid.*, **86**, 1280 (1964).

[6] Y.-N. Tang and F. S. Rowland, *ibid.*, **87**, 3304 (1965).

[7] E. K. C. Lee, Ph.D. Thesis, University of Kansas, 1963.

[8] J. W. Root, Ph.D. Thesis, University of Kansas, 1964.

[9] A. J. Johnston, D. Malcolm-Lawes, D. S. Urch, and M. J. Welch, *Chem. Commun.*, 7, 187 (1966).

[10] F. S. Rowland, E. K. C. Lee, F. Schmidt-Bleek, and Y.-N. Tang, "Symposium on the Kinetics of Pyrolytic Reactions," Ottawa, Canada, 1964, p Q-1.

[11] Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 1625 (1965).

[12] Y.-N. Tang and F. S. Rowland, *ibid.*, **88**, 626 (1966).

[13] An alternative decomposition path also exists for eq 4 in which the products are CHF + TF. This pathway is not of concern to us in these experiments, since the CHF, not containing a radioactive label, is undetected, and the TF does not appear in the radio gas chromatographic analysis procedure used for our experiments.

[14] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

[15] J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

[16] G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4350 (1962).

[17] G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965).

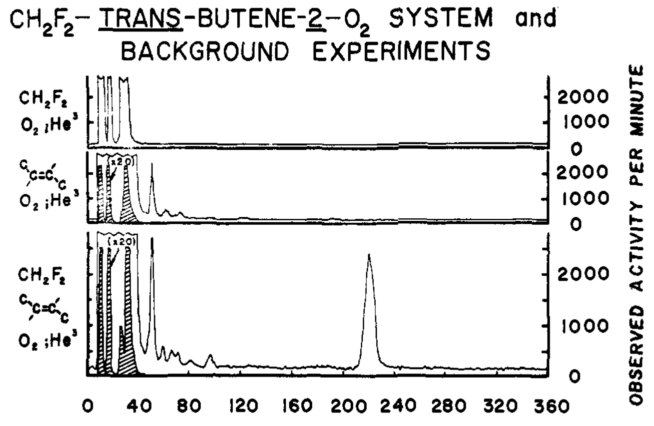

Figure 1. Radioactive products from recoil tritium reactions with CH_2F_2 and *trans*-2-butene. Upper line: $CH_2F_2 + O_2$. Early radioactivity peaks include HT, CH_2TF, $CHTF_2$. No peaks were observed after 50 min. Middle line: *trans*-2-$C_4H_8 + O_2$. Early radioactivity peaks include HT, CH_3T, propene-*t*, etc. No peaks were observed after 90 min. Lower line: Mixture of CH_2F_2 and *trans*-2-$C_4H_8 + O_2$. One prominent additional peak at 220 min corresponds to 1-fluoro-2,3-dimethylcyclopropane-*t*.

scriptions of the procedures for such experiments have been given in the literature.[18-20]

Our techniques are quite similar to those employed by us previously in experiments with methyl chloride and ethyl chloride.[5,6] Gas samples with He^3, CH_2F_2 (or other fluoromethanes), olefins, and other additives were sealed in Pyrex 1720 bulbs of about 12-ml volume; liquid samples of similar organic composition were condensed onto lithium fluoride in capillary tubes. Samples for some preliminary experiments were irradiated for 1 hr in the TRIGA reactor of the Omaha Veterans Administration Hospital with a nominal neutron flux of 10^{11} neutrons/cm^2 sec at a temperature of 20°. The majority of the irradiations were carried out in the nuclear reactor of the Northrop Space Laboratories in Hawthorne, Calif., in an average neutron flux of about 10^{12} neutrons/cm^2 sec for 40 min. The temperature of the samples during irradiation at the Hawthorne reactor depends upon the geometry of the particular irradiation, and has been either ~22 or ~40°. Some experiments were conducted at −12° by immersing the sample bulbs in mixtures of salt, ice, and water during the neutron irradiation.

The radioactive contents of the samples have been separated and assayed by radio gas chromatography.[21,22] This technique has been described in detail, and no changes were made in the operating procedures for these experiments. The separation columns used in the experiments are described in the Appendix.

Chemicals. He^3 was obtained from the Mound Laboratory and purified from its usual tritiated impurities. LiF was obtained from Riedel-DeHaen A. G , Seelze-Hannover, Germany.

CH_2F_2 and CH_2ClF were kindly furnished by Dr. H. L. Jackson of the Du Pont Co. and were used without further purification. No appreciable impurities were observed in gas chromatographic analysis.

The alkenes to C_4, CHF_3, and oxygen were used without further purification as obtained from the Matheson Co. C_2D_4 was obtained from Merck Sharp and Dohme of Canada, Ltd., with an isotopic purity of 99.3%; 2-methyl-2-butene from Matheson Coleman and Bell; 2,3-dimethyl-2-butene from the Chemicals Procurement Laboratories; neon from the J. T. Baker Chemical Co.

Authentic samples of monofluorocyclopropane and 3-fluoropropene for calibration of the gas chromatographic columns were kindly furnished to us by Professor A. F. Trotman-Dickenson.

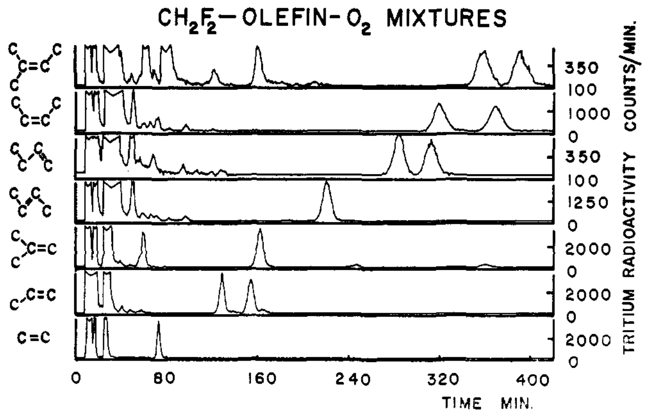

Figure 2. Radioactive products from recoil tritium reactions with CH_2F_2 and various olefins. The peak at 75 min on the bottom line is fluorocyclopropane-*t*; the single or double peaks running from lower left to upper right, beginning with the 75-min peak on the bottom line, are all monofluoroalkylcyclopropane-*t* compounds. The single peak at 720 min from mixtures of CH_2F_2 and tetramethylethylene is not shown.

2-Fluoropropene was obtained from Chemicals Procurement Laboratory.

Identification of Products. The most troublesome experimental aspect in these investigations was the assignment of radioactivity peaks obtained from the radio gas chromatographic analysis. Approximately 10^4 disintegrations, corresponding to 10^{11} molecules, will be recorded during the passage of a typical fluorocyclopropane-*t* peak through the proportional counter detector. At these levels, not enough material existed to permit determination of other physical properties for corroboratory chemical identification. One additional complication also existed: the dozen or so alkyl-substituted fluorocyclopropanes were unavailable commercially and undescribed in the literature.

Our identification of the fluorocyclopropanes is based primarily on internal gas chromatographic evidence, together with the calibration of the retention time of monofluorocyclopropane itself. The identification procedure was based on three separate observational facts.

(a) The radioactive products of recoil tritium reaction in the CH_2F_2–C_2H_4–O_2 system included one peak which coincided on every column tried with the retention time of macroscopic fluorocyclopropane; on several columns, this radioactive peak was shown not to be 3-fluoropropene, the product expected if CTF inserted into the C–H bond of ethylene in analogy with the chemical behavior of CH_2.[14,15]

(b) The radioactive products of recoil tritium reaction in the CH_2F_2–*trans*-2-C_4H_8–O_2 system included one peak not found in CH_2F_2–O_2 or *trans*-2-C_4H_8–O_2, taken separately; this peak occurred in a region of the chromatogram well beyond the locations of any other radioactive peaks, as shown in Figure 1 and had a retention time (220 min) consistent with that expected for 1-fluoro-2,3-dimethylcyclopropane by comparison with fluorocyclopropane (80 min) under the same conditions; and the ratio of the radioactivity in this peak relative to that as $CHTF_2$ was essentially the same as the fluorocyclopropane-*t*/$CHTF_2$ ratio in the C_2H_4 system, as anticipated from reactions 4 and 5 in competition with collisional stabilization.

(c) Similar patterns were observed with other olefins, as shown in Figure 2, for which the yields relative to $CHTF_2$ were also in agreement with the corresponding ratio with ethylene; the number of radioactive peaks in the fluorocyclopropane range is either one, or two of equal size, in agreement with the nonexistence or existence of *syn* and *anti* isomers for the particular fluorocyclopropane. The retention times of the pairs of *syn* and *anti* isomers actually show approximately the same separation on this column for the three pairs differing by one alkyl group (in number of groups *cis* to the F atom), and roughly double the separation for the one pair differing by two alkyl groups.[23]

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[18] See "Chemical Effects of Nuclear Transformations," Vol. 1 and 2, International Atomic Energy Agency, Vienna, 1961; *ibid.*, Vol. 1 and 2, 1965.

[19] R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

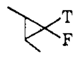
[20] F. Schmidt-Bleek and F. S. Rowland, *Angew. Chem. Intern. Ed. Engl.*, **3**, 769 (1964).

[21] R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

[22] J. K. Lee, E. K. C. Lee, B. Musgrave, Y.-N. Tang, J. W. Root, and F. S. Rowland, *ibid.*, **34**, 741 (1962).

[23] The first peak of each pair is assumed to be *anti*, by analogy with the known behavior of the 1,2-dimethyl compounds. Since the peaks are always approximately equal in size, no conclusions about reaction mechanism are affected by any error in this identification.

Table I. Pressure Dependence of CTF Yield from Recoil Tritium Reactions with CH_2F_2

Total pressure, cm[a]	Yield ratio C_2H_4  /$CHTF_2$	 *trans*-2-C_4H_8  /$CHTF_2$
14	0.51 ± 0.02	0.60 ± 0.02
23	. . .	0.58 ± 0.03
35	0.50 ± 0.02	. . .
78	0.48 ± 0.03	0.45 ± 0.02
164	0.43 ± 0.02	. . .
Liquid phase	. . .	0.07 (I_2) 0.13 (DPPH)

[a] CH_2F_2:olefin = 1:1.

Table II. Yield of CTF from Recoil Tritium Reactions with CH_2F_2–C_2H_4 Mixtures

Pressure, cm				
CH_2F_2	69.5	67.2	36.7	9.4
C_2H_4	4.0	10.5	38.0	63.9
He^3	1.8	1.8	1.8	1.8
O_2	5.6	6.0	5.7	5.1
Total pressure, cm	80.9	85.5	82.2	80.2
 /$CHTF_2$	0.37 ± 0.02	0.48 ± 0.02	0.48 ± 0.03	0.46 ± 0.03
 /C_2H_3T	0.53 ± 0.04	0.086 ± 0.006	0.031 ± 0.002	0.005 ± 0.001

Our over-all identification of the various fluorocyclopropane-*t* molecules is therefore based on the calibration of a single peak with a known, macroscopic sample, and on the appearance of additional peaks which are consistent in number, magnitude, and range of retention time with those expected for the alkylfluorocyclopropanes. We should also add that the appearance of radioactivity peaks in a mixed two-component system, which were not found with either one of the single components taken separately, is quite an unusual phenomenon in recoil tritium investigations, being confined essentially to the present system and the CTCl system in experiments to date.[11,18–20]

Results

Formation of CTF from CH_2F_2. Yield *vs.* Pressure. The formation of CTF as a secondary decomposition product in a recoil tritium system can be demonstrated through a complementary relationship between the yields of CTF and its precursor, the yield of the latter being enhanced by more rapid collisional deexcitation, *i.e.*, by higher pressure or change to liquid phase. The ratios of CTF, as identified through the corresponding fluorocyclopropane-*t*, and $CHTF_2$ are shown for ethylene and *trans*-2-butene in Table I. Both sets of data show the expected trend toward more CTF at lower pressures. The assignment of $CHTF_2^*$ as the precursor rather than CH_2TF^*, which is formed in the system through substitution of T for F, is based on the failure to observe any CTF from the latter when formed by the substitution of T for H in CH_3F. The nonzero ratio (0.10 ± 0.03) in the liquid phase indicates the presence of some $CHTF_2^*$ molecules excited enough to decompose even at these collision frequencies.[3–6]

Formation of CTF from CH_2F_2. Composition Dependence. A series of experiments were run at approximately constant total pressure, while the ratio of CH_2F_2 to C_2H_4 was varied by a factor of 100. As shown in Table II, the ratio $c\text{-}C_3H_4TF/CHTF_2$ is essentially constant over the entire range, even though the ratio of either of these products to that of $CH_2{=}CHT$ (from $T^* + C_2H_4$) changes by about 100. The rough constancy of the $c\text{-}C_3H_4TF/CHTF_2$ ratio indicates that a small amount of ethylene is sufficient to trap almost all of the CTF formed in the system, with little lost to other possible reactions of the CTF. The depression in ratio for the lowest C_2H_4 concentration is real and probably arises from a competition between C_2H_4 and O_2 for reaction with CTF. Since a concentration of O_2 in excess of that of C_2H_4 only reduces the CTF reaction with ethylene to a ratio of 0.37, the reactivity of O_2 with CTF is <0.2 times that of C_2H_4.

The Formation of CTF from Other Fluoromethane Systems. Monofluorocarbene-*t* can also be obtained by recoil tritium reactions with other fluoromethanes, including CH_2ClF and CHF_3, by substitution of T for H and F, respectively.[12] The ratio of fluorocyclopropane-*t* to the labeled precursor molecule is given in Table III for several different sets of experimental conditions.

Table III. The Formation of CTF by Recoil Tritium Reactions with Various Fluoromethanes

Sample compn[a]	Hot atom reaction	Excited precursor	Rel yield[b]
CH_2ClF, C_2H_4, O_2	T for H	$CHTClF^*$	35 ± 2[c]
CHF_3, C_2H_4, O_2	T for F	$CHTF_2^*$	98 ± 8
CH_2F_2, C_2H_4, O_2	T for H	$CHTF_2^*$	48 ± 2
CH_2F_2, C_2H_4	T for H	$CHTF_2^*$	47 ± 2

[a] Total pressure 1 atm. [b] Precursor = 100. [c] Yield of monochlorocyclopropane-*t*, 10 ± 2; total, 45 ± 3.

Recoil tritium atoms will react with CHF_3 to substitute for H or F, forming CTF_3 or $CHTF_2$, respectively. The unimolecular decomposition of CHF_3 has been studied in a single-pulse shock tube, with the conclusion that it decomposes by the elimination of HF.[24] A similar decomposition of CTF_3 will place all of the radioactivity in TF, with no radioactive carbene formed in the process. Consequently, the excited precursor is assumed to be $CHTF_2^*$. The substantially larger decomposition/stabilization ratio for $CHTF_2^*$ from CHF_3 than from CH_2F_2 presumably indicates that the T-for-F reaction in the former cases leaves more residual excitation on the product molecule than does the T-for-H reaction with CH_2F_2.

The excited molecule $CHTClF^*$ undergoes competing modes of decomposition, leading to the formation of CTF + HCl and CTCl + HF, together with the alternate isotopic reactions forming TCl or TF. The ob-

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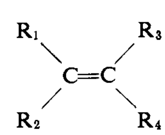
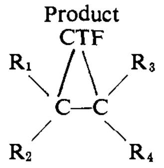
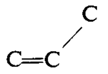
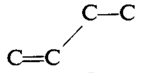
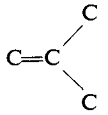
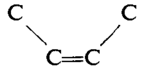
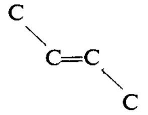
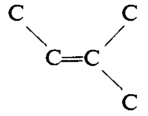
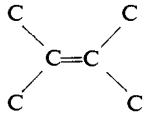
[24] E. Tschuikow-Roux and J. E. Marte, *J. Chem. Phys.*, 42, 2049 (1965).

served preference for the elimination of HCl over HF by a factor of 3.5 is consistent with other observations indicating the preferential elimination of HCl over HF in pyrolysis reactions.[25]

The CH_2F_2–C_2H_4 experiment carried out in the absence of O_2 resulted in a substantial increase in the number of identifiable radioactive products (mostly from radical–radical combination reactions) and of the quantitative yield for many. The ratio of fluorocyclopropane-*t* to $CHTF_2$, however, was unaffected by the deletion of O_2 from the sample contents.

CTF Reactions with Olefins. Recoil tritium reactions have been carried out with mixtures of CH_2F_2–O_2–alkene, utilizing eight different alkenes. The quantitative yields of $CHTF_2$ and the appropriate fluorocyclopropane-*t*, as illustrated in Figure 2, are summarized in Table IV. The ratios are approximately constant (0.45 ± 0.05) for all of the alkenes and indicate that (a) the decomposition pattern of $CHTF_2^*$ is essentially identical in each of the systems (minor differences in ratio could be anticipated, since the larger alkenes should have somewhat larger cross-sections toward stabilization of excited $CHTF_2^*$ molecules); and (b) that the olefins trap an equivalent fraction of the CTF formed in each system, and that this fraction, given the variation in the nature of the olefins, must be approximately unity.

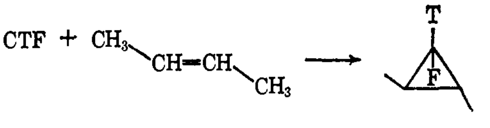
Table IV. Relative Yields of Fluorocyclopropane-*t* and $CHTF_2$ in Recoil Tritium Reactions in the CH_2F_2–Olefin–O_2 System[a]

Olefin 	Product 	*syn*	*anti*
C=C	48 ± 3	...	...
	51 ± 3	25 ± 2	26 ± 2
	46 ± 3	24 ± 2	22 ± 2
	54 ± 5	...	...
	48 ± 2	24 ± 1	24 ± 1
	45 ± 2	...	...
	40 ± 5	20 ± 3	20 ± 3
	41 ± 5	...	...

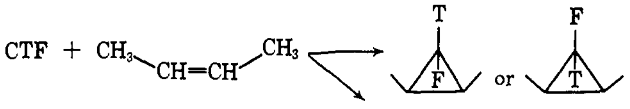
[a] CH_2F_2:alkene:O_2 = 1.0:0.4:0.07; total pressure, 1 atm; yield of $CHTF_2$ = 100.

Table IV also indicates that, in all of the cases for which two epimers are possible, they are found in equal yields, within the accuracy of measurement. Obviously, there is no tendency for the reacting CTF radical to rotate into any particular directional orientation relative to the alkyl substituents on the olefinic reactant. A similar lack of stereospecificity has been observed with pyrolytic CHCl and CHBr.[17]

Stereospecific Addition of CTF to 2-Butenes. Completely stereospecific, single-step addition of CTF to an olefin would require that alkyl groups maintain the orientation relative to each other that existed in the reacting olefin. Under these conditions, each of the three isomers of 1-fluoro-2,3-dimethylcyclopropane-*t* would be formed by reaction of CTF with only one of the two 2-butenes, as indicated in eq 6 and 7. The experimental results, listed in Table V, are in complete accord with the stereospecific mechanism outlined here.

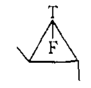
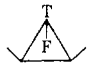
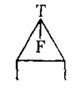


(6)



(7)

Table V. Stereospecific Addition of CTF to 2-Butenes

Sample composition	Rel yield of product[a] 		
CH_2F_2, *trans*-2-C_4H_8, O_2, He^3	45 ± 2	0.4 ± 0.4	0.3 ± 0.3
CH_2F_2, *cis*-2-C_4H_8, O_2, He^3	0.5 ± 0.5	24 ± 1	24 ± 1
CH_2F_2, *cis*-2-C_4H_8, neon (81%), He^3, O_2	0.1 ± 0.5	24 ± 2	25 ± 2

[a] $CHTF_2$ = 100; all samples at 1 atm total pressure.

One experiment, also listed in Table V, was also carried out in the presence of a large excess of neon, which was included to provide an inert moderator which might facilitate singlet–triplet interconversion for the CTF. The results indicate no such effect for neon gas on CTF–olefin systems.

Relative Reactivities of Olefins toward CTF. While the reactivity of olefins is sufficient toward CTF to ensure that all of the latter will be "caught" in these experiments, the reactivities of the olefins do not need to be identical, and in fact are not. Two separate experiments have been performed to evaluate the relative reactivities of olefins. In one series, several olefins were present simultaneously and assay of the individual fluorocyclopropane-*t* peaks permitted estimates of the relative reactivity of each such olefin. Since these mixtures are relatively complex, with many products of recoil tritium reaction with each olefin, as well as those formed by the CTF–olefin reaction, the

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[25] M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1962.

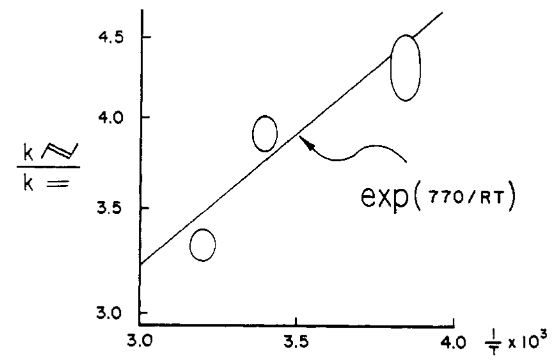
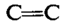
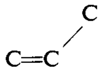
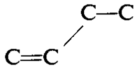
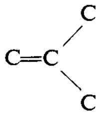
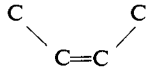
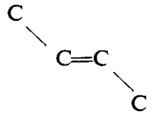
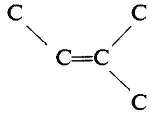
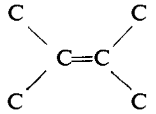


Figure 3. Temperature dependence of relative reactivities per mole of CTF with *trans*-2-butene and ethylene. The ovals represent approximate error limits for the measurement of both temperature and relative reactivities.

accuracy of comparison is not particularly high. The second series of experiments involved binary competition between ethylene and each of the other olefins in turn, giving relatively simple gas chromatographic spectra and permitting a more accurate analysis of the relative yields. Both types of data, in excellent agreement with each other, are shown in Table VI.

Table VI. Relative Yields of Fluorocyclopropanes from CTF Reactions with Olefins (~22°)

Olefin	Rel yields (*vs.* C_2H_4)	Rel yields (direct competition, normalized to *trans*-2-C_4H_8)
	1.00	...
	2.06 ± 0.08[a]	2.20 ± 0.18
	2.03 ± 0.06[a]	
	2.79 ± 0.07	
	3.02 ± 0.08[a]	3.02 ± 0.24
	3.90 ± 0.05	(3.90)
	4.13 ± 0.12[a]	
	5.87 ± 0.18	

[a] Sum of yields of two epimers in equal amounts.

Isotope Effect on Olefin Reactivity with CTF. C_2H_4 *vs.* C_2D_4. An isotopic difference in the reactivity of C_2H_4 and C_2D_4 cannot be directly tested in the absence of a good gas chromatographic separation for the resultant *c*-C_3H_4TF and *c*-C_3D_4TF molecules. However, an indirect test can readily be carried out through comparison of reactivities *vs.* a common olefin, in this case *trans*-2-butene. In experiments carried out simultaneously at 40°, the ratio of reactivities, as measured through the yields of the corresponding fluorocyclopropane-*t* molecules, were *trans*-2-C_4H_8/C_2H_4 = 3.32 ± 0.07, and *trans*-2-C_4H_8/C_2D_4 = 3.93 ± 0.12. The reactivity of C_2H_4 toward CTF is thus 1.18 ± 0.04 times as great as that of C_2D_4.

Temperature Effect on the Relative Reactivities of Olefins. The competition between C_2H_4 and *trans*-2-C_4H_8 has been studied at three temperatures, and, as shown in Table VII, a small temperature dependence has been observed. The measurements of the temperature of irradiation are not very accurate, since the temperature of the irradiation facility will change with continued operation of the reactor. Within the accuracy involved (and the probable error in temperature is larger than the probable error in reactivity ratios), the entire reactivity difference can be accounted for with an activation energy for reaction between CTF and C_2H_4 770 cal/mole higher than that for CTF with *trans*-2-butene. An Arrhenius plot of the average values is shown in Figure 3.

Table VII. Relative Reactivity of Ethylene and *trans*-2-Butene toward CTF at Different Temperatures

Approx temp, °C	
40	3.32 ± 0.07
22	3.94 ± 0.12 3.87 ± 0.22
−12	4.35 ± 0.22 4.27 ± 0.26

Absence of CTF Insertion Reactions. Absence of Isomerization of Fluorocyclopropanes. A special search was made for the radioactivity of 3-fluoropropene, the expected product from direct insertion of CTF into the C–H bond of ethylene, in analogy with the well-established insertion reactions of singlet CH_2. An upper limit on the amount of 3-fluoropropene-*t* has been established as ≤0.001, relative to the observed yield of fluorocyclopropane-*t* as 1.00. Search for the other fluoropropenes also gave negative results. Since all four fluoropropenes are formed during the isomerization of highly excited fluorocyclopropane,[26] we conclude that the addition of CTF to ethylene did not release sufficient energy to the product molecule to permit isomerization to the fluoropropenes.

Discussion

Stereospecificity of CTF Reactions with Olefins. The observation that carbenes frequently react with a high degree of stereospecificity with olefinic substrates has led to the widely used and accepted criterion that stereospecific reactions are evidence for the singlet electronic state of the reacting carbene.[27] A corollary to this hypothesis is that the stereospecificity results from the simultaneous formation of both of the C–C bonds in the product cyclopropane. Numerous liquid-

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(26) F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3655 (1964); 1141 (1965).

(27) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

phase experiments exist for which essentially complete stereospecificity has been observed in the formation of the cyclopropane compound, although a number of these are systems for which it is now clear that the reacting species was not the free carbene itself.[14,15] In addition, if a carbene reacted with an olefin to form a trimethylene-type intermediate, the presence of the solvent cage and solvent molecules might very well hinder free rotation about the newly created single bonds and preserve stereospecificity even though the two C–C bonds to the carbene were not formed simultaneously.

Gas-phase experiments have the advantage that there can be no solvent hindrance to free rotation, and the reactions of CF_2 with 2-butene have been shown to be completely stereospecific, consistent with singlet CF_2 reaction.[28] The great bulk of gas-phase experiments have been conducted with CH_2 as the carbene, and, although strong stereochemical preferences have been observed, a yield has always been observable for those products anticipated from nonstereospecific reaction.[29,30] Such gas-phase experiments with methylene are complicated by two factors, each of which can be a source of a nonstereospecific reaction component: (a) gas-phase photolysis of ketene, diazomethane, etc., leads to the formation of two kinds of carbene, one of which (in yields as high as 30%) does not react stereospecifically, and is usually identified therefore as the triplet carbene; (b) addition of CH_2 to an olefin produces an excited molecule whose excitation energy is sufficiently high (estimated as 101 kcal/mole for singlet CH_2 + C_2H_4)[31] that secondary isomerizations can occur, leading to the formation of the same products anticipated from nonstereospecific interactions. Such reactions can be substantially reduced by increasing the pressure at which the experiments are conducted, but readily measurable yields from isomerization are still obtained at 40 atm total pressure for cyclopropane formed from methylene plus ethylene.[31]

The reactions of CTF with *cis*- and *trans*-2-butene, however, furnish a direct measurement of the yields of the stereospecific products, and show that these reactions are completely stereospecific within the accuracy of the measurements, *i.e.*, 100 ± 1% in each case. The CTF–olefin reaction system therefore represents a clear-cut, gas-phase example in which stereospecificity is completely retained. The observations further imply that the reaction involves either (a) the simultaneous formation of both C–C bonds, or (b) that the rate of ring closure must be two or more orders of magnitude faster than the rate of rotation around the C–C bonds formed in the first step; the simultaneous formation of both bonds is much the more probable explanation.

No preference has been found for the formation of *syn* or *anti* epimers with any of the olefins for which they exist, in agreement with the observations of Closs and Coyle of CHCl and CHBr formed by thermolysis of $ClCHN_2$ and $BrCHN_2$.[17] Our results in the gas phase confirm the conclusions of Closs and Coyle in the liquid phase: the lack of stereoselectivity for *syn* or *anti* epimers is characteristic of the free monohalocarbene. Those reaction systems showing a *syn*/*anti* ratio > 1 must therefore be reacting through an intermediate other than the free monohalocarbene. The observation of competitive reaction ratios as large as 6 requires, as a minimum, several collisions on the average for reaction, and makes it quite unlikely that the reacting species possesses excess internal energy, again in agreement with the conclusions of Closs and Coyle.[17]

Electronic State of CTF. No physical evidence concerning the electronic states of monohalocarbenes, *e.g.*, spectroscopic observations, has yet been published, and only chemical evidence is available for use in the assignment of the electronic state of the CTF formed in our experiments. The chemical evidence all indicates that the CTF is present in the singlet electronic state: (a) reaction with olefins is completely stereospecific; (b) the reacting carbene is quite insensitive to the presence of O_2, which is very effective in eliminating the reaction products formed by triplet methylene.[29,31,32]

Furthermore, judging from the lack of change in the observed stereospecificity of reaction with the inclusion of excess neon, we draw the conclusion that the singlet is also the ground electronic state. The singlet state has already been established to be the ground state for the dihalocarbenes.[14,15]

Absence of Insertion Reaction with Ethylene. Recent measurements of the reactions of singlet CHT indicate that 24% of the reactions with ethylene proceed through the mechanism of insertion into the C—H bond of the ethylene to form $CH_2TCH{=}CH_2$.[31] Although the corresponding insertion reaction of CTF should lead to the formation of 3-fluoropropene-*t*, none of the latter was found in these experiments. No additional information is available from our experiments to indicate why monofluorocarbene will not undergo the insertion reaction so typical of the unsubstituted carbene itself. Closs and Coyle have already reported that CHCl does not readily insert into C–H bonds and exhibits a strong preference for insertion into weaker C–H bonds when it does insert.[16,17]

Excitation Energy of CTF Reactions with Olefins. The addition of singlet CHT to ethylene creates molecules of cyclopropane-*t* so excited that the competition between isomerization to propylene-*t* and stabilization by collision is approximately equal at a total pressure of 190 cm. Application of RRKM theory to the isomerization of cyclopropane-*t* leads to an estimate of 101 kcal/mole as the excitation energy of that addition reaction.[31] Although the rate parameters for the unimolecular isomerization of fluorocyclopropane-*t* are not very different from those of cyclopropane-*t*,[33] no isomerization has been observed at 1 atm pressure for fluorocyclopropane-*t*. From the upper limit of 0.1% for the fraction of fluorocyclopropane-*t* undergoing isomerization, an upper limit of 75 kcal/mole can be placed upon the excitation energy released from the

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(28) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 758 (1965).

(29) H. M. Frey, *Progr. Reaction Kinetics*, **2**, 131 (1964).

(30) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(31) C. F. McKnight, E. K. C. Lee, and F. S. Rowland, *J. Am. Chem. Soc.*, **89**, 469 (1967). Some numbers have been slightly changed because of minor data adjustments.

(32) Since the intervention of O_2 in this reaction scheme is believed usually to occur *after* the initial carbene reaction with the olefin, but before further reaction of the initially formed product, the argument is less direct—O_2 removes the stable reaction products formed by the reaction of triplet methylene with the olefin; see C. F. McKnight and F. S. Rowland, *ibid.*, **88**, 3179 (1966).

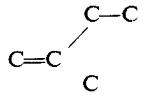
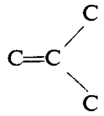
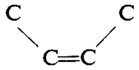
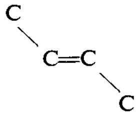
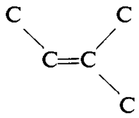
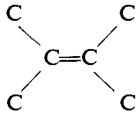
(33) For monofluorocyclopropane,[26] $A = 3.8 \times 10^{14}$ sec^{-1} and $E_{act} = 61.0 \pm 0.7$ kcal/mole. For cyclopropane, $A = 1.5 \times 10^{15}$ sec^{-1} and $E_{act} = 65.0$ kcal/mole.

addition of CTF to ethylene. This maximum of 75 kcal/mole indicates that the fluorine atom has stabilized the singlet carbene by more than 25 kcal/mole relative to the unsubstituted carbene.[34]

Heats of formation are not available for CHF or for c-C_3H_5F. Rough estimates of these values can be made by assuming that $\Delta H_f°$ for CHF is the arithmetic mean of the values of CH_2 (85 ± 3)[35] and CF_2 (−35 ± 10)[36] ($\Delta H_f° \sim 25 \pm 6$ kcal/mole), and that the difference in heats of formation of c-C_3H_5F and c-C_3H_6 (13) will be the same as for CH_3F (−59)[37] and CH_4 (−18) ($\Delta H_f°$(c-C_3H_5F) ~ -28 kcal/mole). From these two heats of formation, the exothermicity of the addition of CTF to ethylene can be crudely estimated as 65 kcal/mole, in accord with the experimental estimate of ≤ 75 kcal/mole.

Factors Affecting Olefin Reactivity toward CTF. The chemical reactivity of various olefins toward CTF increases by a factor of 6 between ethylene and tetramethylene, as shown in Table VI. The values fall in the same order as for other experiments with mono- and dihalocarbenes, as shown in Table VIII, except for the observations with the relatively inert CF_2.[28,38] The nucleophilicity of the olefins is increased by increasing numbers of alkyl substituents, and this is reflected in an increasing reactivity toward the electrophilic carbene. The experimental evidence concerning the temperature effect in our system suggests that most, if not all, of this difference in reactivity results from a difference in the activation energy for the reaction. Very probably the C_2H_4/C_2D_4 isotope effect is also largely a consequence of a lower activation energy for reaction with the former. The increased selectivity may represent a higher activation energy for CTF reaction with olefins than for CHCl or CHBr. The selectivity of reaction of CF_2 is so great that additional study of its competitive reactions with other olefins would be very desirable.

Table VIII. Relative Reactivities of Olefins toward Addition Reactions by Various Halocarbenes[a]

	CTF[b]	CHCl[17]	CHBr[17]	CCl_2[14]	CBr_2[14]
	0.73	0.74	0.75	...	...
	1.00	1.00	1.00	1.00	1.00
	1.08	0.99	1.02	...[c]	...
	1.40	1.09	1.10	...	...
	1.48	1.18	...	2.9	3.2
	2.10	1.20	1.18	6.6	3.5

[a] Normalized to isobutylene = 1.00. [b] This work. [c] CF_2 reacts 12.8 times more rapidly with isobutylene then with *cis*-2-butene.[28]

Our experiments show that the effect of a methyl and of an ethyl substituent are very nearly equal, while two methyl substituents have a much greater effect than one ethyl substituent. Comparison of the results observed with *cis*-2-C_4H_8, *trans*-2-C_4H_8, and isobutylene indicates that the geometry of the methyl groups relative to one another has a marked effect on the nucleophilicity of the olefinic group. In our experiments, however, the effects of alkyl substituents on the electron distribution of the olefin seem to overshadow completely any steric hindrance effects such as those reported for CCl_2.[39]

Acknowledgments. We thank Professor A. F. Trotman-Dickenson and Dr. H. L. Jackson for gifts of fluorocarbons necessary for these experiments.

Appendix

Gas Chromatographic Columns Used for Analysis. The majority of the ethylene-containing samples were analyzed with the following three columns in separate aliquots. The products are listed in the observed order of elution from each column, with unseparated peaks bracketed together. In order to resolve all the major products from the reacting systems, the use of all three columns is usually necessary.

(a) 50'DMS: 50-ft column of 35% dimethylsulfolane on 30–60 mesh Chromosorb, operated at 25°. Products: (H_2 + CH_4 + CF_4), (C_2H_6 + C_2H_4), C_3H_8, (CH_3F + CHF_3), C_3H_6, (i-C_4H_{10} + C_2H_3F), n-C_4H_{10}, (c-C_3H_6 + C_2H_2 + CH_2F_2 + C_2H_5F), 1-C_4H_8, i-C_4H_8, $CH_3CHF{=}CH_2$, *trans*-2-C_4H_8, *trans*-C_3H_5F, *cis*-2-C_4H_8, *cis*-C_3H_5F, butadiene, n-C_3H_7F, $CH_2FCH{=}CH_2$, c-C_3H_5F, 2-methyl-2-butene, CH_2ClF.

(b) 50'Saf: 50-ft column of 35% Safrole on 30–60 mesh Chromosorb P, operated at 0°. Products: (H_2 + CH_4 + CF_4), CHF_3 (C_2H_4 + C_2H_6), (CH_3F + C_2H_2), (C_2H_3F + CH_2F_2), C_3H_8, C_3H_6, C_2H_5F, i-C_4H_{10}, (c-C_3H_6 + $CH_3CHF{=}CH_2$), *trans*-C_3H_5F, n-C_4H_{10}, *cis*-C_3H_5F, 1-C_4H_8, i-C_4H_8, *trans*-C_4H_8, (*cis*-C_4H_8 + n-C_3H_7F), $CH_2FCH{=}CH_2$, c-C_3H_5F.

(c) 50'PCA: 50-ft column of 10% propylene carbonate on 30–50 mesh activated alumina, operated at 0°. Products: H_2, CH_4, CF_4 (CH_3F + C_2H_4), C_2H_6, C_2H_2, CH_2F_2, CHF_3, C_3H_6, c-C_3H_6, C_3H_8, CH_2ClF, c-C_3H_5F.

For samples containing other alkenes and also for some of the ethylene samples, an additional column was employed for the analysis of higher fluorocyclo-

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(34) Both the 101- and 75-kcal/mole figures would include any vibrational energy of the carbene; in both systems, this contribution is likely to be small (<5 kcal/mole).

(35) J. A. Bell and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **84**, 3417 (1962).

(36) L. Brewer, J. L. Margrave, R. F. Porter, and K. Wieland, *J. Phys. Chem.*, **65**, 1913 (1961).

(37) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966.

(38) The total spread in reactivity with olefins observed for CHCl and CHBr represents an increase of only 60% from 1-butene to tetramethylethylene, in experiments carried out at −30° in solution. Our experiments, covering the range from C_2D_4 to tetramethylene show a factor of 7 at 22°, and would be expected to rise to a factor of 10–15 if carried out at −30°.

(39) O. M. Nefedov, M. N. Manakov, and A. A. Ivaschenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1242 (1962).

propanes. Normally, the first aliquot of each sample, consisting of about 50% of the total, was analyzed on this column. Two or more of the other columns were then used for auxiliary purposes.

(d) 30′DMS: 30-ft column of 25% dimethylsulfolane on 30–50 mesh activated alumina. The order of the retention times is similar to that of the 50′DMS, but the actual time required is much shorter. With a flow rate of 25 ml/min, it takes more than 10 hr for the elution of oxygenated compounds such as alcohols.

Two more columns, a 50-ft di-*n*-butyl phthalate (50′DBP) and a 50-ft tri-*o*-tolyl phosphate (50′TTP), were also used during the preliminary runs. They were discarded later because the oxygenated compounds emerged too quickly, making impossible the isolation of the individual peaks of the fluorocyclopropanes.

Analysis of Mixtures from Competition Experiments. The relative reactivities of different olefins were obtained from the observed yields of the appropriate radioactive product(s) for each olefin, corrected for the mole ratio of the olefins in the mixture. The mole ratios were measured by thermal conductivity response, calibrated for each molecule, as measured during the gas chromatographic analyses.

Kinetics of the Hydroxymercuration of Olefins[1]

Jack Halpern and H. Burnham Tinker

Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637. *Received June 16, 1967*

Abstract: The kinetics of the hydroxymercuration of 20 olefins and substituted (hydroxy, chloro, and cyano) olefins, $Hg^{2+} + {>}C{=}C{<} + H_2O \rightarrow [Hg{\geqslant}C{-}C{\leqslant}OH]^+ + H^+$, have been determined in aqueous perchloric acid solution. The rate law in each case was found to be rate $= k[Hg^{2+}][{>}C{=}C{<}]$, where the values of k, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ for ethylene are 5.1×10^3 M^{-1} sec^{-1} (at 25°), 9.2 kcal/mole, and -10 eu, respectively. The rate of hydroxymercuration was found to be independent of the H^+ concentration (between 0.001 and 0.1 M), to increase with the $NaClO_4$ concentration, and, contrary to earlier reports, to be unaffected by H_2O_2 and by O_2. For substituted olefins an excellent correlation between log k and Taft's σ^* ($\rho^* = -3.3$) was observed, suggesting a transition state with considerable carbonium ion character. No evidence was found for mercury(II)–olefin π complex (mercurinium ion) intermediates and, while the possibility of such intermediates is not excluded, the data do permit certain limits to be placed upon their stabilities and concentrations.

The addition of oxy salts of mercury to olefins (oxymercuration) to give β-oxyorganomercury(II) derivatives is a well-known reaction,[2–5] which finds no really close parallel in the chemistry of other metals.[6–8] The reaction in aqueous solutions containing uncomplexed mercury(II) (hydroxymercuration) is, typically

$$Hg^{2+} + CH_2{=}CHR + H_2O \longrightarrow [HgCH_2CHROH]^+ + H^+ \quad (1)$$

where R = H, alkyl, or aryl. While the stoichiometry and stereochemistry of the reaction have been extensively investigated,[3,5] there are virtually no reliable data[9] concerning its kinetics, apparently because the reaction in solutions containing uncomplexed Hg^{2+} is generally too fast for conventional rate measurements.

In this paper we report the results of such kinetic measurements on the hydroxymercuration of ethylene and some 20 other olefins and substituted (hydroxy, chloro, and cyano) olefins, made by means of the stopped-flow method. The measurements were made, in part, with a view to seeking evidence for a mercury(II)–olefin π complex (mercurinium ion), which has been postulated as an intermediate in oxymercuration and deoxymercuration reactions.[10,11] but no such evidence was obtained.

Of related interest to the present study are earlier reports on the kinetics of oxymercuration of olefins in solutions containing complexed mercury(II) (*e.g.*, chloride, acetate, and pyridine complexes)[12] on the kinetics of acid-induced deoxymercuration[11,13] and on the kinetics of the oxidation of olefins by thallium(III) for which a mechanism involving an oxythallation step, analogous to oxymercuration, has been proposed.[7,8]

Experimental Section

Materials. The gaseous olefins (ethylene, propylene, 1-butene, isobutene, *cis*-2-butene, and *trans*-2-butene) were all Matheson CP grade reagents. The absence of volatile impurities was con-

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(1) This work was supported by grants from the National Science Foundation, the Advanced Research Projects Agency, and the Petroleum Research Fund, administered by the American Chemical Society.

(2) K. Hofmann and J. Sand, *Chem. Ber.*, **33**, 1340, 2692 (1900).

(3) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

(4) G. F. Wright, *Ann. N. Y. Acad. Sci.*, **65**, 436 (1957).

(5) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).

(6) Possible exceptions to this generalization are to be found in the reactions of certain thallium(III) salts with olefins.[7,8]

(7) P. M. Henry, *J. Am. Chem. Soc.*, **87**, 990, 4424 (1965); **88**, 1597 (1966).

(8) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961); C. B. Anderson and S. Winstein, *ibid.*, **28**, 605 (1963); H. J. Kabbe, *Ann.*, **656**, 204 (1962).

(9) In the light of the results reported in this paper it would appear that most of the earlier rate measurements on the hydroxymercuration of olefins in solutions containing uncomplexed Hg^{2+}, such as those of P. Brandt and O. Plum [*Acta Chem. Scand.*, **7**, 97 (1953)], refer to physically transport limited, rather than chemically determined, rates.

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(11) See, for example, M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, **30**, 373 (1965), and references cited therein.

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