[Contribution from the Department of Chemistry, University of Kansas]

Addition and Abstraction Reactions of the Trichloromethyl Radical with Olefins

EARL S. HUYSER

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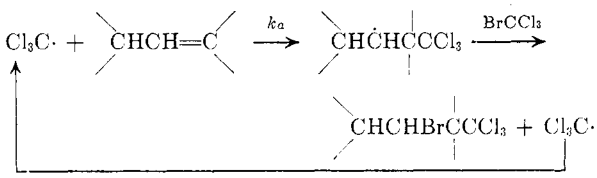
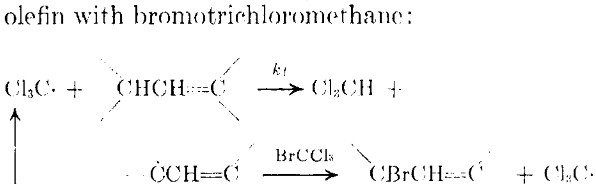
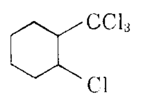
In reactions with olefins, the trichloromethyl radical both adds to the double bond and abstracts allylic hydrogens. The latter reaction is evidenced by the formation of chloroform and allylic halides in the reactions of certain olefins with carbon tetrachloride and bromotrichloromethane. The ratio of the rate of addition of the trichloromethyl radical to the double bond with respect to the rate of hydrogen abstraction, k_a/k_t, has been found for a number of olefins. The values of these ratios are discussed in terms of the structure of the olefin.

In Kharasch additions of carbon tetrachloride and bromotrichloromethane, the trichloromethyl radical adds to the unsaturated linkage of the olefin in a chain propagating reaction.[1] These same polyhalomethanes have been used to halogenate various hydrocarbons,[2] alcohols,[3] and aldehydes.[4] In these reactions, a hydrogen atom is abstracted by a trichloromethyl radical in a radical chain propagating reaction. The lability of allylic hydrogens toward abstraction by a free radical suggests the possibility of the following chain sequence for reaction of an olefin with bromotrichloromethane:

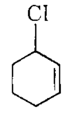




Evidence of such allylic attack by a trichloromethyl radical has been reported for cyclohexene. The peroxide induced reaction of this olefin with carbon tetrachloride results in the formation of both the expected addition product I and the halogenated olefin II.[5] Likewise, the formation of a low boiling product along with the expected addition product in the reaction of cyclohexene and bromotrichloromethane[6] suggests the formation of an allylic bromide in this case as well. The present investigation was undertaken to determine the effect of structure in olefins on the relative amounts of addition and hydrogen abstraction by the trichloromethyl radical occurring in their photochemically induced reactions with bromotrichloromethane.



I



II

CALCULATIONS

The ratio of the reaction rate constants, k_a/k_t, a measure of the relative reactivity of the double bond of an olefin with respect to the allylic hydrogens toward attack by a trichloromethyl radical, can be determined from the stoichiometry of the overall reaction of bromotrichloromethane with an olefin. Both chain sequences require one molecule of bromotrichloromethane for each reaction of a trichloromethyl radical. However, each reaction of this radical involving hydrogen abstraction results in the formation of a molecule of chloroform. The reactivity ratio k_a/k_t can be ascertained by determining the amount of bromotrichloromethane that has reacted and the amount of chloroform produced in the overall reaction. It is necessary to maintain a high mole ratio of the olefin to bromotrichloromethane to minimize interaction of the trichloromethyl radical with the reaction products.

$$k_a/k_t = \frac{\text{moles of BrCCl}_3\text{ reacted} - \text{moles of HCCl}_3\text{ formed}}{\text{moles of HCCl}_3\text{ formed}}$$

The numerator in this equation is the quantity of bromotrichloromethane consumed in the addition reaction and the denominator is the amount in-

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(1) C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, pp. 247–253.

(2) J. P. West and L. Schmerling, U. S. Patents **2,553,799** and **2,553,800** (1951); Y. A. Ol'dekop, *Doklady Akad. Nauk SSSR*, **93**, 75 (1953); E. I. Heiba and L. C. Anderson, *J. Am. Chem. Soc.*, **79**, 494 (1957); E. S. Huyser, *ibid.*, **82**, 391 (1960).

(3) G. A. Razuvaev and N. S. Vasiliesky, *Doklady Akad. Nauk SSSR*, **80**, 69 (1951); G. A. Razuvaev and Y. A. Sorokin, *Zhur. Obshchei Khim.*, **23**, 1519 (1953); G. A. Razuvaev, B. N. Moryganov and A. S. Volkova, *Zhur Obshchei Khim* **25**, 495 (1955); J. W. Heberling, Jr., and W. B. *Soc.*, **78**, 5433 (1956). McCormack, *J. Am. Chem.*

(4) S. Winstein and F. H. Seubold, Jr., *J. Am. Chem. Soc.* 69, 2916 (1947).

(5) E. C. Kooyman and E. Farenhorst, *Rec. trav. chim.*, **70**, 867 (1951); S. Israelashvili and J. Shabatay, *J. Chem. Soc.*, 3261 (1951).

(6) M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

volved in the hydrogen abstraction reaction. The necessary data are readily obtained by gas chromatographic analyses of the reaction mixtures (see Experimental).

RESULTS AND DISCUSSION

The following table lists the values of k_a/k_t determined by the method outlined above for a number of olefins. The agreement between various experiments with the same olefin is satisfactory, the observed deviations resulting largely from analytical limitations of the method used for these experiments. The decrease in the ratio k_a/k_t with increase in reaction temperature for a given olefin is indicative of the higher activation energy requirement for the hydrogen abstraction reaction with respect to that of the addition reaction.

TABLE I

Relative Amount of Addition to the Double Bond with Respect to Hydrogen Abstraction by a Trichloromethyl Radical for Various Olefins

Olefin	Temp.	k_a/k_t	No. of Runs	Average Deviation	Column[a]
1-Octene	77.8	43	3	3	O[b]
1-Decene	77.8	44	3	5	S[c]
2-Pentene	77.8	5.7	3	0.1	S
3-Heptene	77.8	3.5	4	0.1	S
3-Heptene	40.0	5.0	4	0.2	S
4-Methyl-2-pentene	77.8	1.26	2	0.02	S
4-Methyl-2-pentene	40.0	1.68	3	0.04	S
cis-2-Butene	99.	34	4	1.0	K[d]
trans-2-Butene	99.	26	4	1.5	K
Cyclohexene	77.8	1.20	4	0.03	S
Cyclohexene	40.0	1.85	8	0.04	S, K
Cyclopentene	77.8	5.4	2	0.2	S
Cyclopentene	40.0	6.5	4	0.2	S
Cycloheptene	77.8	5.5	2	0.1	O
Cycloheptene	40.0	8.3	3	0.1	O

[a] See Experimental for details concerning the gas chromatographic analysis. [b] Liquid phase, Oronite No. 16. [c] Liquid phase, Silicone 550. [d] Liquid phase, Kel-F Grease.

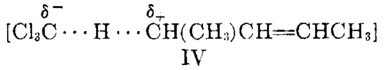
As the data obtained for 1-octene and 1-decene indicate, the amount of hydrogen abstraction by the trichloromethyl radical with respect to addition is comparatively small. This result is consistent with the fact that in free radical additions of polyhalomethanes to terminal olefins, essentially no side products are detected. However, hydrogen abstraction is an important reaction of the trichloromethyl radical in non-terminal olefins such as 2-pentene and 3-heptene. In these olefins, the addition of the radical to the double bond is sterically hindered. The comparatively low k_a/k_t values in nonterminal olefins very likely results from a decrease in k_a rather than from an increase in k_t.

A comparison of the k_a/k_t values for a series of nonterminal olefins indicates what may be a difference in the reactivity of certain hydrogens toward abstraction by a trichloromethyl radical. The 2-butenes, having only primary allylic hydrogens, undergo little hydrogen abstraction by a trichloromethyl radical in comparison to addition to the double bond. 2-Pentene, with two allylic hydrogens on a secondary carbon, suffers a considerable amount of hydrogen abstraction. It seems unlikely that steric interference to addition in 2-pentene would be so much greater than that in 2-butene that this factor alone could account for this difference, whereas, previous work[7] has shown that secondary hydrogens are more easily abstracted than primary hydrogens by a trichloromethyl radical. Thus, it is more probable that a marked increase in the value of k_t in 2-pentene over that in 2-butene rather than a decrease in k_a accounts for the observed difference in the k_a/k_t values for these olefins. The increase in the amount of hydrogen abstraction with respect to addition found for 3-heptene in comparison to 2-pentene may very likely be statistical, the 3-heptene having four secondary allylic hydrogens whereas the 2-pentene has two. In the case of 4-methyl-2-pentene, an olefin with a tertiary hydrogen in an allylic position, a relatively large amount of hydrogen abstraction occurs in its reactions with trichloromethyl radicals.

This order of reactivity of hydrogens toward abstraction by a trichloromethyl radical very likely results in part from the decrease in the bond dissociation energy of the involved carbon-hydrogen bond due to resonance stabilization of the resulting free radical.[8] However, the influence of polar factors on the rates of hydrogen abstraction by a trichloromethyl radical may also be important in determining the relative reactivity of primary, secondary and tertiary hydrogens in these reactions. A transition state in which the trichloromethyl radical assumes carbanion-like character and the carbon in the substrate from which the hydrogen is being abstracted assumes carbonium ion-like character has been suggested for abstractions of benzylic hydrogens.[9] Transition states III, IV and V might be suggested for the allylic hydrogen abstraction reactions for 2-butene, 2-pentene and 4-methyl-2-pentene, respectively.

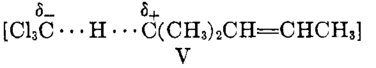
$$[Cl_3\overset{\delta_-}{C}\cdots H\cdots \overset{\delta_+}{C}H_2CH{=}CHCH_3]$$

III



$$[Cl_3\overset{\delta^-}{C}\cdots H\cdots \overset{\delta_+}{C}H(CH_3)CH{=}CHCH_3]$$

IV



$$[Cl_3\overset{\delta_-}{C}\cdots H\cdots \overset{\delta_+}{C}(CH_3)_2CH{=}CHCH_3]$$

V

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(7) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 5246 (1960).

(8) For discussion of radical stabilization see Ref. 1, pp. 51–53.

(9) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

As the order of stability of carbonium ions is tertiary > secondary > primary, the ease of attainment of these transitions states would be III < IV < V.

The k_a/k_t values for *cis*- and *trans*-2-butene suggest that either hydrogen abstraction is faster for the *trans* olefin than for the *cis*, or, possibly addition of the trichloromethyl radical to the *cis* isomer is faster than to the *trans*. Crowding of the methyl groups in *cis*-2-butene has been suggested by Szwarc[10] to lower the reactivity of the allylic hydrogens of this compound toward abstraction by a free radical. However, data reported for the relative amounts of addition of a methyl radical to *cis*- and *trans*-2-butene with respect to allylic hydrogen abstraction ($k_a/k_t = 3.3$ for *cis*-2-butene and 6.9 for *trans*-2-butene)[10] are not consistent with this suggestion. Further, Walling[11] reports a slightly higher reactivity of *cis*-2-butene over *trans*-2-butene toward abstraction of allylic hydrogens by *tert*-butoxy radicals. Thus, a faster hydrogen abstraction reaction for the *trans* olefin does not find support in other reactions. On the other hand, Skell and Woodworth found that at 0° *cis*-2-butene, the less stable of the two isomers, was more reactive toward addition by a trichloromethyl radical than the more stable *trans*-2-butene by a factor of 2.4.[12] Assuming the value of k_t is approximately the same for *cis*- and *trans*-2-butene with the trichloromethyl radical at 99°, the data obtained in the present study indicate that the *cis* isomer is more reactive toward addition than the *trans* isomer by a factor of 1.3 at this temperature. The higher reaction temperature could account for the difference in the ratios of reactivity of the two olefins toward addition by the trichloromethyl radical.

The amount of hydrogen abstraction in cyclohexene is greater than expected for an internal olefin with four secondary allylic hydrogens (compared, for example with 3-heptene). This somewhat unexpected behavior of cyclohexene in these reactions may result from conformational effects. Addition to this cyclic olefin may be hindered by the unfavorable axial approach to the double bond[13] by the comparatively large trichloromethyl radical. On the other hand, two of the allylic hydrogens are in quasi-equatorial positions[14] and are favorably situated for approach by the trichloromethyl radical.

The k_a/k_t values found for cyclopentene, when compared with those of either 3-heptene or cyclohexene, are higher than might be expected. Further, on the basis of conformational strain resulting from bond opposition in this five-membered ring,[15] one might predict a slow rate for the addition of the radical, a reaction which would increase bond opposition, in comparison to hydrogen abstraction, a reaction which would relieve bond opposition strain. The k_a/k_t values found for cyclopentene indicate the opposite is very likely true. The relief of internal angular strain might be suggested to account for the observed results. In the addition reaction, the conversion of one of the two sp^2 hybridized carbons to an sp^3 hybridization would relieve angular strain whereas the formation of a planar allylic radical in the hydrogen abstraction reaction would increase angular strain. The effect of these factors might be expected to influence the ease of attaining the transition states of the two reactions, lowering the activation energy requirement for the addition reaction and increasing that for the hydrogen abstraction reaction. It is questionable whether similar factors can be suggested for the high k_a/k_t values found for cycloheptene. However, a similarity in kinetic behavior of cycloheptane and cyclopentane derivatives and the somewhat anomalous behavior of cyclohexane derivatives has been observed in other reactions.[16]

EXPERIMENTAL

Materials and equipment. Bromotrichloromethane (The Dow Chemical Co.), was redistilled under vacuum (n_D^{25} 1.5032) until it gave one peak on gas chromatographic analysis. The following olefins were used without further purification and all gave one peak on gas chromatographic analysis: 2-pentene (Phillips, Pure Grade)[17]; 4-methyl-2-pentene (Phillips, Pure Grade)[17]; *cis*-2-butene (Matheson); *trans*-2-butene (Matheson); cyclohexene (Matheson Coleman and Bell); cyclopentene (Matheson Coleman and Bell). The following olefins were redistilled until they gave one gas chromatographic peak: 1-octene (Matheson Coleman and Bell); 1-decene (The Connecticut Hard Rubber Co.); 3-heptene (Matheson Coleman and Bell). Cycloheptene (b.p. 114°, n_D^{25} 1.4563) was prepared by the dehydration of cycloheptanol obtained from the potassium borohydride reduction of cycloheptanone (Aldrich Chemical Co., Inc.). Gas chromatographic analysis of the cycloheptene indicated a minimum purity of 99%.

The reactions were conducted in a Pyrex tube fitted with a spherical joint and cap which was clamped tight during the heating and illumination period. The reactions involving the 2-butenes were performed in sealed Pyrex tubes. Temperature control was maintained by means of a constant temperature water bath (40°), an ethanol vapor bath (77.8°) and a water vapor bath (99°). All reactions were initiated by illumination of the reaction mixtures with a 275-watt General Electric sun lamp.

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[10] R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Am. Chem. Soc.*, **78,** 5557 (1956).

[11] C. Walling, Abstracts, Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash. (1959), p. 86.

[12] P. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **79,** 4638 (1955).

[13] H. L. Goering and L. L. Sims, *J. Am. Chem. Soc.*, **77,** 3465 (1955).

[14] D. H. R. Barton, R. C. Cookson, W. Klyne, and C. W. Shoppee, *Chem. & Ind.*, 21 (1954).

[15] For discussion of these conformational effects in five-membered ring compounds, see E. L. Eliel, *Steric Effects in Organic Chemistry*, Ed., M. S. Newman, Wiley, New York, 1956, pp. 121–122.

[16] H. C. Brown, *Rec. Chem. Progr. Kresge-Hooker Sci. Lib.*, **14,** 83 (1953).

[17] *Cis* and *trans* isomers both present and were not separated by the gas chromatographic technique used in the determinations.

Columns used for the gas chromatographic analysis, depending on the requirements of the particular reaction mixture, were the following: a 7-foot, 1/4-inch column packed with 15% Silicone 550 (Dow Corning Corp.) on Chromosorb W; a 12-foot, 1/4-inch column packed with 12% Kel-F Grease (Minnesota Mining and Manufacturing Co.) on Chromosorb W; and a 10-foot, 1/4-inch column packed with 15% Oronite No. 16 (Oronite Chemical Co.) on Chromosorb W. The column temperature in each case was 78° with helium used as the carrier gas (helium head pressure, 10 p.s.i.g.). The samples were introduced unto the column with a 0.010 ml. pipette through a Fisher sample injection valve.

Experimental procedure. About 2 ml. of the olefin and 0.5 ml. of bromotrichloromethane were pipetted into the reaction tube. A 0.010-ml. sample of this mixture was analysed by gas chromatography and the area of the bromotrichloromethane peak measured with a planar compensating planimeter. The tube was sealed and placed in the constant temperature bath and allowed to reach thermal equilibrium. The tube and its contents were then illuminated by the sun lamp, which was placed about 15 to 20 in. from the bath to exclude any external heating from the lamp, for a period of 5–20 min. in order to allow about 50–75% of the bromotrichloromethane to react. The tube was removed from the bath and allowed to reach room temperature and a 0.010-ml. sample was analysed by gas chromatography under conditions identical to those employed for the first sample. The areas of the bromotrichloromethane and chloroform were determined with a planimeter and the chloroform area corrected to the same molar area as the bromotrichloromethane (correction factor, $BrCCl_3/HCCl_3 = 1.18$). The decrease in the bromotrichloromethane area was the total bromotrichloromethane reacted. The corrected chloroform area was taken as the amount of this bromotrichloromethane involved in the hydrogen abstraction reaction. The difference in the decrease in the bromotrichloromethane area and the corrected chloroform area was the amount of bromotrichloromethane that reacted in the addition reaction. Typical data are shown in Table II.

TABLE II

GAS CHROMATOGRAPHIC DATA COLLECTED TO DETERMINE k_a/k_t

			Areas (Cm.^{2})				
			$BrCCl_3$		$HCCl_3$		
Olefin	Temp.	Run	Before	After	Found	Corrected	k_a/k_t
3-Heptene	77.8	3	42.0	31.2	2.0	2.4	3.5
	77.8	4	39.5	20.9	3.5	4.2	3.4
Cycylpentene	40.0	2	43.1	6.6	4.1	4.9	6.4
	40.0	4	54.8	20.0	3.8	4.6	6.6

The reactions with the 2-butenes were carried out in the presence of benzene which served as an internal standard for the gas chromatographic analyses of the reaction mixtures.

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LAWRENCE, KAN.

[CONTRIBUTION FROM THE PHILLIPS PETROLEUM CO.]

The Radiation-Induced Reaction of Aldehydes with Olefins

C. E. STOOPS AND C. L. FURROW

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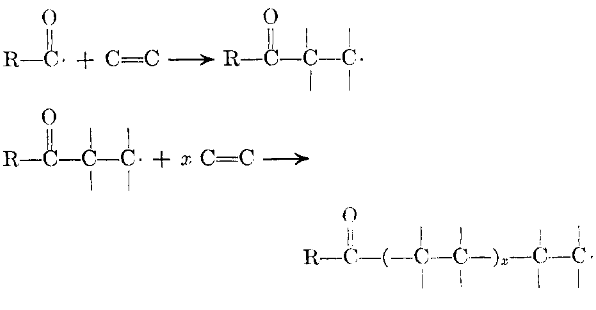
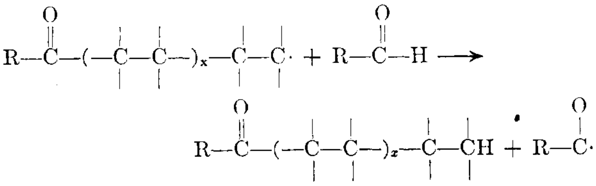
The radiation-induced reaction of aldehydes with olefins yields low molecular weight ketones by a chain process in which the acyl radical derived from the aldehyde adds to an olefin molecule with subsequent chain growth or with chain transfer to regenerate the acyl radical. Reactivity declines progressively in the series acetaldehyde, propionaldehyde, isobutyraldehyde, trimethylacetaldehyde, and also in the series ethylene, propylene, *trans*-butene-2, *cis*-butene-2, isobutylene. Quantitative estimation of yield was made by conversion of each product mixture to 2,4-dinitrophenylhydrazones followed by spectrophotometric determination of the individual quantities of each derivative after separation by paper chromatography. Conclusions regarding structure-reactivity relations are made.

The preparation of ketones by the free radical addition of aldehydes to olefins, with the acyl radical effectively the chain-carrying species, has been recognized for some time.[1]



$$R-\overset{O}{\overset{\|}{C}}\cdot + C{=}C \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot$$

$$R-\overset{O}{\overset{\|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot + x\,C{=}C \longrightarrow R-\overset{O}{\overset{\|}{C}}-(-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-)_x-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot$$



$$R-\overset{O}{\overset{\|}{C}}-(-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-)_x-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot + R-\overset{O}{\overset{\|}{C}}-H \longrightarrow R-\overset{O}{\overset{\|}{C}}-(-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-)_x-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}H + R-\overset{O}{\overset{|}{C}}\cdot$$

The predominant radiation-induced reaction of aldehydes with olefins has been found to follow the same course.[2] Structure-reactivity relations were

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[1] Cheves Walling, *Free Radicals in Solution,* Wiley New York, 1957, pp. 273–278.

[2] Since completion of this work a report has appeared concerning the radiation-induced addition of aldehydes to esters of unsaturated acids: R. H. Wiley and J. R. Harrell, *J. Org. Chem.*, **25**, 903 (1960).