lower in benzene than in chlorobenzene and lower still in carbon tetrachloride.[2] Also it has been reported that for cumyl radical, a is 0.25 in benzene at 40° but is 0.35 in cyclohexane.[3a] Thus eq 7 predicts the direction of change and for cumyl radical is very close to the right order of magnitude. If we assume that carbon tetrachloride and cyclohexane are essentially nonsolvating toward the 2-cyano-2-propyl radical, eq 7 would predict a twofold increase in k_t in going from cyclohexane to benzene solution. If carbon tetrachloride interacts more strongly with the radical than cyclohexane, eq 7 predicts a greater than twofold increase in k_t.

Table IX. Effect of Solvent on Radical Termination Constants

Radical	Solvent	Method	$k_t \times 10^{-9}$ M^{-1} sec^{-1}
Cumyl	Benzene	I[a]	8
	Cyclohexane	I	8
2-Cyano-2-propyl	Benzene	I, II[b]	0.94
	Cyclohexane	I	4
	Hexafluorobenzene	I, II	0.48
t-Butyl	Benzene	II	0.73
	Cyclohexane	II	2.2
Cyclohexyl	Benzene	II	0.8[c]
	Cyclohexane	II	0.8[c]

[a] Method I involves only the comparison of derivative peak heights. [b] Method II consists of determining k_t absolutely independently in each solvent. [c] From ref 7.

If solvent effects are responsible for the poor agreement between measured and calculated a values for the cyanopropyl radical, we must assume that considerable recombination of radicals produced from azobisisobutyronitrile must occur before the radicals arrive at an equilibrium state of solvation. This hypothesis would in turn imply that the rate-limiting step in some recombination reactions may be some kind of solute–solvent relaxation process. With some trepidation we suggest that the seemingly anomalous reactivity relationships discussed above may ultimately be attributable to this effect.

Acknowledgment. We would like to thank Professors P. D. Bartlett, J. R. Shelton, and J. M. McBride, and Dr. F. Haupt for their generous gifts of the azo compounds used in this study. We also thank Professor J. D. Roberts for the use of his CAT 4000 and Mr. E. J. Hamilton for his work in design of the experimental system. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479.

The Nature of the Transition State in the Oxidation of Olefins by Chromium(VI)[1]

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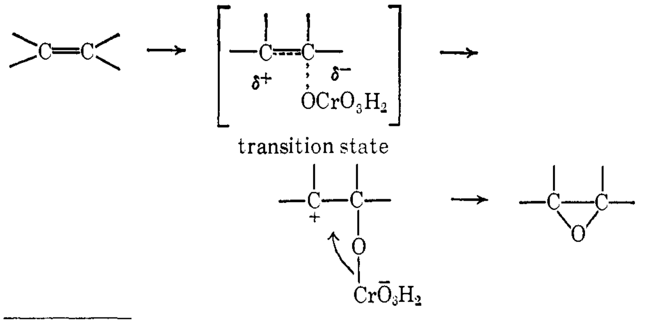
Abstract: The rate of oxidation of olefins by chromic acid is determined by the total number of alkyl substituents on the double bond rather than by the degree of substitution at the most highly substituted terminus. This suggests a symmetrical structure for the transition state of the rate-limiting step of the oxidation. The relative reactivities of cyclopentene and norbornene with respect to cyclohexene are low and fall into the category characteristic for reactions with three-membered transitions states. It is therefore concluded that an epoxide is the first oxidation product and that it is formed directly from the olefin and chromium(VI).

A considerable number of studies has been devoted to the oxidation of olefins by chromic acid under a variety of conditions.[3] In a number of cases epoxides have been isolated from the oxidation and many of the products of a higher oxidation level which have been obtained could be rationalized in terms of epoxide intermediates. Nevertheless, serious arguments against the intermediacy of epoxides have been raised.[4]

Even if epoxides are intermediates in the oxidation of olefins by chromic acid, it is by no means clear whether they are formed in a reaction with chromium(VI) or whether they originate from a reaction involving either chromium(V) or chromium(IV). Further, if they are formed in the reaction of chromium(VI) and the olefin, are they formed in the rate-limiting step or as secondary products *via* an intermediate carbonium ion (Scheme I)[3,5] or cyclic chromium(IV) ester (Scheme II)?[3]

Scheme I



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(1) This work was supported by grants of the National Science Foundation and of the U. S. Army Research Office, Durham, N. C.

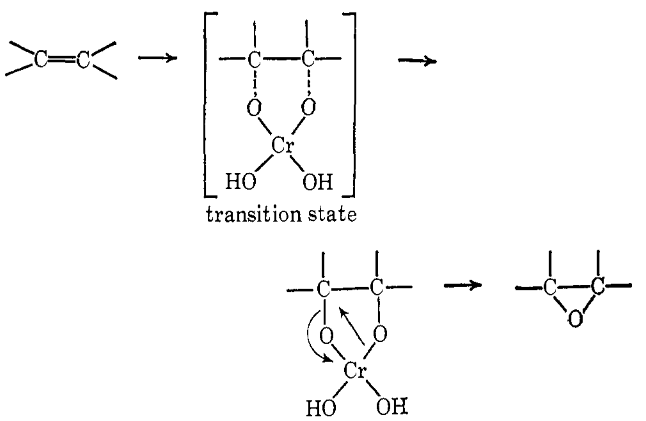
(2) To whom inquiries should be directed.

(3) The subject has recently been carefully and critically reviewed, K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965.

(4) M. A. Davis and S. J. Hickinbottom, *J. Chem. Soc.*, 2205 (1958).

(5) An analogous mechanism leading to a free radical could be formulated for a one-electron oxidation. However, there is at the present time little reason to believe that a one-electron oxidation does in fact take place. Moreover, the approach used in the discussion of the carbonium ion mechanism can be applied in an analogous way to the free-radical mechanism.

Scheme II



The carbonium ion mechanism (Scheme I) differs from both the formation of a cyclic ester (Scheme II) or from the direct formation of an epoxide by proceeding by way of a nonsymmetrical transition state. The remaining two mechanisms differ by the size of the cyclic transition state. In order to gain a clearer understanding of the reaction taking place in the rate-limiting step of the chromic acid oxidation of olefins an investigation of the effect of structure on oxidation rates was undertaken. As the intermediate chromium valence states (chromium(IV) and (V)) react faster than chromium(VI), all information obtained from kinetic studies refers to chromium(VI) only. Thus, unlike reaction product studies, reaction rate measurements yield results reflecting only the reactivity of chromium(VI) despite the fact that two thirds of the products are formed in subsequent reactions involving intermediate chromium valence states.

Our approach is based on the study of symmetrical and nonsymmetrical substitution using the method first introduced by Bartlett and Sargent[6] in the study of the formation of the norbornyl cation *via* the π route. Further, we attempted to gain information about the ring size of the cyclic transition state by comparing relative reactivities for some cyclic olefins. In this approach we made use of an idea recently applied by Bingham, Meakins, and Whitham[7] to the investigation of the mechanism of epoxidation.

The oxidation of olefins by chromium(VI) is first order in olefin and chromium, acid catalyzed, and solvent dependent.[8] Since the oxidation has been observed to be accelerated by light[9] and our preliminary measurements showed that oxidation rates of at least some olefins are increased in the presence of oxygen, all measurements were carried out under standard conditions with the exclusion of oxygen and light.

Chromic acid oxidations of olefins usually yield complex mixtures of reaction products highly dependent on the reaction conditions employed. Diols and mono- and diacetates have been isolated[10] besides epoxides from oxidations in acetic acid solutions. Due to their high reactivity most of the primary reaction products are usually obtained only in low yields and considerable amounts of higher oxidation products are formed.

The oxidation of olefins with chromic acid also yields considerable amounts of products derived from oxidation at the allylic position.[3] However, evidence presented in this work as well as obtained in other studies[11] suggests that allylic oxidation is due to the presence of intermediate valence states of chromium and does not represent a reaction of chromium(VI) itself. We are therefore confident that the kinetic data which we have obtained refer solely to the reaction between chromium(VI) and the double bond of the olefin.

Results and Discussion

The results of our measurements in 95% acetic acid in the absence of air and light at 25° are summarized in Table I. No value for ethylene is given because the rate of the uncatalyzed oxidation is too slow to be measured under the reaction conditions which we selected.[12]

Table I. Rates of the Chromium(VI) Oxidation of Olefins at 25° in 0.002 *M* Sulfuric Acid in 95% w/w Acetic Acid in the Absence of Air and Light

Olefin	10^2k, M^{-1} min^{-1}
$CH_2{=}CH_2$	Very slow
Monosubstituted Ethylenes	
$CH_3CH{=}CH_2$	0.95[a]
$CH_3CH_2CH{=}CH_2$	1.53
$CH_3CH_2CH_2CH{=}CH_2$	2.22
$CH_3CH_2CH_2CH_2CH{=}CH_2$	2.94
$CH_3CH_2CH_2CH_2CH_2CH{=}CH_2$	2.77
$(CH_3)_3CCH{=}CH_2$	2.02
Disubstituted Ethylenes	
$(CH_3)_2C{=}CH_2$	7.28
$(CH_3)_3CCH_2\underset{\underset{CH_3}{\mid}}{C}{=}CCH_2$	10.1
cis-$CH_3CH{=}CHCH_3$	8.42
trans-$CH_3CH{=}CHCH_3$	5.55
trans-$CH_3CH_2CH{=}CHCH_3$	7.24
trans-$CH_3CH_2CH_2CH{=}CHCH_3$	8.18
Tri- and Tetrasubstituted Ethylenes	
$(CH_3)_2C{=}CHCH_3$	91.9
$(CH_3)_2C{=}CHC(CH_3)_3$	32.4
$(CH_3)_2C{=}C(CH_3)_2$	469
Cyclic Olefins	
Cyclohexene	72.4
Cyclopentene	93.1
Norbornene	397
Styrenes	
$C_6H_5CH{=}CH_2$	167
$(C_6H_5)_2C{=}CH_2$	363
cis-$C_6H_5CH{=}CHC_6H_5$	56.4
trans-$C_6H_5CH{=}CHC_6H_5$	221

[a] Estimated from rate in 0.02 *M* H_2SO_4 for propene ($k = 3.97 \times 10^{-2}$) and isobutene ($k = 30.5 \times 10^{-2}$).

The number of available allylic hydrogens seems to be without any effect on the over-all rate of the oxidation reaction: *t*-butylethylene is oxidized faster than pro-

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(6) P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, 87, 1297 (1965).

(7) K. D. Bingham, G. D. Meakins, and G. H. Whitham, *Chem. Commun.*, 445 (1966).

(8) A. Rahman, M.S. Thesis, The Catholic University of America, Washington, D. C., 1965.

(9) J. Roček and A. Rahman, unpublished results.

(10) J. Roček and J. Drozd, unpublished results.

(11) P. Müller and J. Roček, to be published.

(12) Ethylene is oxidized fairly rapidly in the presence of air. In the presence of small amounts of air the oxidation in a closed system comes to a standstill after some time, but will continue further if more air is injected. No other olefin showed a similarly dramatic sensitivity to the presence of air during the oxidation.

Table II. Relative Reactivities of Substituted Ethylenes

Olefin	Ag complex formation	$PdCl_4^{2-}$ oxidation	Acid-catalyzed hydration	Tl^{3+} oxidation	Hydroxymercuration	Epoxidation	Br_2 addition	Cl_2 addition	Br atom addition	Cr(IV) oxidation
$CH_2{=}CH_2$	2.4	3.8		6×10^{-3}	0.051	0.045	0.016		0.056	Very slow
$CH_3CH{=}CH_2$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00[a]	1.00	1.00
cis-$CH_3CH{=}CHCH_3$	0.59	0.32	1.68	0.35	0.058	22	43	63	5.4	8.9
trans-$CH_3CH{=}CHCH_3$	0.15	0.36	0.71	0.08	0.017		28	50	5.7	5.9
$(CH_3)_2C{=}CH_2$	0.43	Very slow	10^3–10^4	1.2×10^3	Very fast	22	89	58	22	7.7
$(CH_3)_2C{=}CHCH_3$	0.088		10^3–10^4			230	1500	1.1×10^4		97
$(CH_3)_2C{=}C(CH_3)_2$	0.01					Very fast		4.3×10^5		490
Reference	14	15	21	22	23	16	17, 18	19	25	*b*

[a] 1-Butene. [b] This work.

pene and 1-butene, and norbornene is much more reactive than cyclopentene. This is in agreement with our assumption that little or no allylic oxidation takes place in the rate-limiting step (*i.e.*, by chromium(VI) oxidation).

The reaction does not seem to be very sensitive to steric effects. *t*-Butylethylene and α-neopentyl-α-methylethylene exhibit reactivities characteristic of similarly substituted olefins containing no bulky groups. Tetramethylethylene is the most reactive olefin of all which we investigated. Here a still somewhat higher reactivity might have been anticipated based on simple extrapolation; it is therefore possible that a small steric retardation is observed in this case. The largest rate effect which can be ascribed to steric hindrance is observed in the case of α-*t*-butyl-β,β-dimethylethylene which reacts almost three times slower than trimethylethylene.

Thus, as in the chromium(VI) oxidation of paraffins,[13] steric effects in the oxidation of olefins are of only minor importance. In this respect the chromium(VI) oxidation of olefins differs diametrically from the ability of olefins to form complexes with silver ions[14] or from the oxidation of olefins with palladium(II) chloride,[15] in which cases steric effects seem to be dominant (*cf.* Table II). The high sensitivity to steric effects in the formation of Ag^+ complexes and in the Pd(II) oxidation is believed to be the result of the formation of direct metal to carbon bonds. The insensitivity of the chromium(VI) oxidation to steric effects thus makes any formation of a direct chromium to carbon bond in the transition state unlikely.

The rate of the oxidation increases with the increasing number of alkyl substituents. Longer and more highly branched substituents in general lead to a greater rate enhancement. The rate of the oxidation is determined primarily by the number of alkyl substituents rather than by their position on the double bond. Thus *cis*- and *trans*-2-butenes and isobutene react at about the same rate. In this respect the chromium(VI) oxidation resembles closely epoxidation[16] and bromine[17,18] and chlorine[19] addition to olefins, *i.e.*, reactions leading to a three-membered ring product or intermediate.[20] On the other hand, the reaction differs diametrically from the acid-catalyzed hydration,[21] or from the oxidation of olefins with thalic ions.[22] In both of these reactions isobutene is ~10^3–10^4 times more reactive than the 2-butenes and the reaction proceeds through a carbonium ion type intermediate. A similarly high reactivity of isobutene compared with *cis*- and *trans*-2-butenes was recently observed also in the hydroxymercuration of olefins.[23] In the latter reactions the electrophile attacks the double bond unsymmetrically leading to a transition state with a developing cationic center. The rate of these reactions is then determined by the stability of the incipient carbonium ion and, hence, by the degree of substitution on the more highly substituted terminus of the double bond.[24]

The conclusion which can be drawn from the finding that the reactivity *vs.* structure dependence in the chromium(VI) oxidation of olefins falls so clearly into the first group of reactions (Table II) is that the transition state for this reaction like that for epoxidation, bromination, and chlorination must be symmetrical. We can thus exclude any acyclic mechanism of the type shown in Scheme I as well as cyclic but nonsymmetrical mechanisms.

Both the three-membered transition state leading to an epoxide and the five-membered transition state leading to a chromium(IV) ester of a vicinal diol are symmetrical. A tentative distinction between these two alternatives can be reached on the basis of the relative reactivity of some cyclic olefins. Garbisch and coworkers[26] have shown in their elegant computation that cyclopentene and norbornene are more strained than cyclohexene by about 3.7 and 9.7 kcal/mol, respectively, and that a considerable part of this strain is relieved in a cyclic transition state leading to a saturated compound. Based on this approach they could quantitatively cal-

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(19) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965).

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(23) J. Halpern and H. B. Tinker, *ibid.*, **89**, 6427 (1967).

(24) A basically similar situation is found also in the addition of bromine atoms to olefins to form a bromoalkyl radical.[25]

(25) P. I. Abel, *Trans. Faraday Soc.*, **60**, 2214 (1964).

(26) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Am. Chem. Soc.*, **87**, 2932 (1965).

Table III. Relative Reactivities of Cyclopentene and Norbornene in Reaction with Cyclic Transition States

Reaction	Ref	Size of cyclic transition state	Reactivity ratio Cyclopentene: cyclohexene	Norbornene: cyclohexene
Diimide reduction	26	6	15.5	450
Diphenylnitrilimine addition	27	5	12	280
Benzonitrile oxide addition	27	5	19	1800
Phenyl azide addition	7, 27	5	64	6500
Picryl azide addition	7	5		8000
Diethylaluminum hydride addition	28	4	9.4	
Hydroboration	29	4	110	
Epoxidation	7, 16	3	1.5	1.2
Bromination	30	3	1.4	
CBr_2 addition	31	3	1.25	
Ag^+ complex formation	14	3	2.0[a]	17
Cr(VI) oxidation	*b*		1.29	5.5

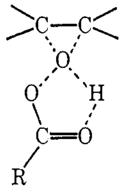
[a] Ratio of stability compounds. [b] This work.

culate the relative rates for the diimide reduction of these and a large number of other olefins.

The high reactivity of cyclopentene and norbornene relative to cyclohexene is not restricted to the diimide reduction, but seems to be shared by a number of other reactions as long as they go through a four-, five-, or six-membered cyclic transition state. Norbornene exhibits extremely high reactivities in 1,3-dipolar addition reactions.[27] Cyclopentene is considerably more reactive than cyclohexane not only in dipolar addition reactions[27] with a five-membered transition state but even toward diethylaluminum hydride[28] or disiamylborane[29] in reactions which presumably proceed with a four-membered transition state.

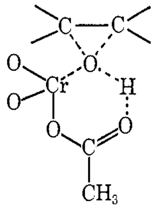
As a three-membered ring is considerably strained one would not expect that the transformation of a double bond into a three-membered ring would lead to a significant relief of steric strain. Indeed relatively small differences in reactivities for strained and unstrained olefins are observed for reactions like epoxidation,[7,16] bromination,[30] or the addition of a dibromocarbene[31] to the double bond (Table III). For reactions leading to a three-membered cyclic product or intermediate the relative reactivities with respect to cyclohexene are between 1.25 and 2.0 for cyclopentene and 1.2 and 17 for norbornene, whereas for reactions with larger cyclic transition states the figures are between 9.4 and 110 for cyclopentene and 450 and 8000 for norbornene. Our own results for the chromium(VI) oxidation of olefins fall clearly into the first category.

The conclusions which can be drawn from our results lead us thus to believe that the rate-limiting step in the chromic acid oxidation of an olefin is a symmetric electrophilic attack of chromium(VI) on the double bond leading to an epoxide. Although the transition state for the reaction could be formulated in several different ways, it seems attractive to formulate the reaction similarly to the epoxidation of olefins by peracids for which transition state **1** has been suggested.[32]



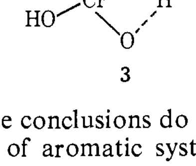
1

The mechanism has the advantage that it assumes that the oxygen transferred to the olefin comes from an OH group which is certainly more electrophilic than a nonprotonated oxygen and also allows the proton to be transferred intramolecularly by an unstrained cyclic mechanism. In acetic acid solutions chromic acid is known to exist predominantly in the form of its monoacetate[33] and the reaction may proceed through transition state **2**.

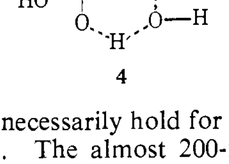


2

As there seems to be no basic difference in the way chromic acid oxidations proceed in acetic acid solutions and in aqueous solutions one may be permitted to speculate that epoxides could be formed in aqueous solutions by way of transition state **3** or **4**.



3



4

These conclusions do not necessarily hold for the oxidation of aromatic systems. The almost 200-fold in-

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(31) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

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crease in reactivity from propene to styrene is unique for the chromium(VI) oxidation and is not found either for the oxidation with peracids[16] or for the bromination[34] reaction (Table IV). It may well indicate a change in mechanism due, perhaps, to the high ability of the aromatic ring to stabilize a positive charge. We thus do not feel that mechanism I can be excluded for the oxidation of styrene and other unsaturated aromatic compounds until more data on these systems is available.[35]

Table IV. Reactivities of Substituted Styrenes Relative to 1-Propene

Olefin	Cr(IV)	CH_3CO_3H	Br_2
$C_6H_5CH{=}CH_2$	167	2.7	2.2
cis-$C_6H_5CH{=}CHC_6H_5$	56.4	2.6	0.024
trans-$C_6H_5CH{=}CHC_6H_5$	221	1.2	0.018
$(C_6H_5)_2C{=}CH_2$	363	11.4	55
Reference	*a*	16	34

[a] This work.

Experimental Section

Acetic Acid. Fisher ACS reagent (99.7%) was diluted with water to 95% (w/w).

Chromic Acid. The solutions in 95% (w/w) aqueous acetic acid were prepared from anhydrous chromium trioxide; the concentrations were determined spectrophotometrically at 350 mμ.

Olefins. The gaseous olefins (ethylene, propylene, 1-butene, isobutene, *cis*-2-butene, and *trans*-2-butene) were obtained commercially from Phillips Petroleum (Research Grade, minimum purity 99.8 mol %).

Liquid Olefins. The following commercially available olefins were used: 2-methyl-2-butene, 2,3-dimethyl-2-butene, 1-pentene (Baker Grade Reagent), 1-hexene (Phillips Pure Grade, purity 99.4 mol %, 0.6% of a mixture of *cis*- and *trans*-2-hexenes and *cis*- and *trans*-3-hexenes), *t*-butylethylene and cyclopentene (Columbia Organic Chemicals, 95% pure), cyclohexene (Phillips Petroleum, Pure Grade, 99.3 mol % cyclohexene, 0.7% cyclohexane), 2,4,4-trimethyl-2-pentene (Phillips Petroleum Technical Grade, purity 96 mol %, 3.8% 2,4,4-trimethyl-1-pentene, 0.2% isoctenes), 2,4,4-trimethyl-1-pentene (Phillips Petroleum, Pure Grade, 0.95% 2,4,4-trimethyl-2-pentene), 1,1-diphenylethylene, *cis*-stilbene, 1-heptene (puriss.), *trans*-2-pentene, and *trans*-2-hexene (Aldrich Chemical Co.). Their purity was checked by glpc and they were subjected to several purification procedures, including column distillation, purification by preparative glpc, and vacuum line distillation over sodium metal. It was found that the oxidation of olefins is sensitive to peroxidic impurities. Rate measurements on freshly distilled samples lead invariably to lower values than when samples or solutions prepared in advance were used. The lowest rates and most consistent results were obtained for samples freshly distilled in a vacuum line over sodium metal. This procedure was then generally adopted. The data in Table I have been obtained or have been rechecked using this procedure.

Solid Olefins. Norbornene (Aldrich Chemical Co.) was twice sublimed and vacuum distilled, mp 45° (lit.[37] 44–44.5°). *trans*-Stilbene (Eastman Organic, "Scintillation Grade") was used without purification.

Apparatus. The apparatus (Figure 1) consisted of a 50-ml, 24/40 standard joint flask equipped with a magnetic stirrer and a side opening covered by a rubber septum. The flask was connected by a manifold to the steel cylinder with the compressed or liquid olefin, a thin rubber balloon of about 500-ml capacity serving as a gas reservoir, an open water manometer, a water aspirator, and an oil pump. The flask and the manifold up to stopcocks B and C were covered with a heavy coat of black paint. The flask was immersed in a thermostated bath.

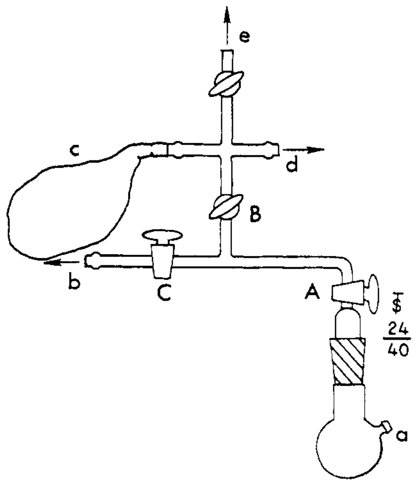

Figure 1. Apparatus for solubility and rate measurements for gaseous olefins: a, rubber septum; b, connection to manometer, water aspirator, and oil pump; c, rubber balloon; d, open-end manometer; e, connection to gas cylinder.

Solubility Measurements. After the manifold was purged several times with the olefin, the flask containing 5 ml of 95% (w/w) acetic acid or of a solution of sulfuric acid in 95% acetic acid was attached, and the whole system was evacuated with a water aspirator, filled with the olefin, and evacuated again.

The system was then filled with the olefin, the olefin pressure adjusted to 1–1.5 cm of water above the atmospheric pressure, and the solvent saturated for 20–25 min at 25 ± 0.1° under vigorous stirring. The olefin content in the solution was analyzed by withdrawing a sample of the saturated solution by a syringe and injecting a known volume into a solution of a known amount of bromine in 95% acetic acid in a 5-ml volumetric flask and determining the final bromine concentration spectrophotometrically at 450 mμ (isobestic point for Br_2–Br_3^-). The method was checked using solutions of cyclohexene and styrene of comparable concentrations and turned to give results with an accuracy of ±5%.

The solubility for each olefin was determined at least in two to five runs. The solubility listed in Table V and used for the calculation of the second-order rate constants are average values. The maximum deviation of an individual measurement from the average value was 10%.

Table V. Solubility in 95% AcOH (w/w) at 25° in 10^2 *M*

	H_2SO_4, *M*		
Olefin	0	0.002	0.02
$CH_2{=}CH_2$	3.10		4.00
$CH_3CH{=}CH_2$	16.1		23.3
$CH_3CH_2CH{=}CH_2$		70.1	
cis-$CH_3CH{=}CHCH_3$	89.3	118	
trans-$CH_3CH{=}CHCH_3$	69.8	95.5	
$(CH_3)_2C{=}CH_2$	57.1	75.8	83.3

The solubilities were found to be somewhat dependent on the acidity, the values obtained in the absence of sulfuric acid being consistently lower by about 30%.

Kinetic Measurements. a. Gaseous Olefins. The kinetic measurements were carried out in the same manner as was described in the determination of solubilities, except for using a larger amount of acetic acid (25–30 ml) and an additional evacuation of the system by an oil pump (flask cooled in liquid nitrogen) to remove remaining traces of air completely. After reaching the temperature of the thermostat, the olefin pressure was again adjusted to 1–1.5 cm of water above the atmospheric pressure.

The oxidation was started by injecting a solution of chromic acid

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(34) J. E. Dubois and A. Schwarcz, *Compt. Rend.*, **259**, 2227 (1964).

(35) A product possessing a considerable degree of carbonium ion character has recently been suggested even for the addition of bromine to some substituted styrenes in order to explain the lack of observed stereospecificity.[36]

(36) R. C. Fahey and H. J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968).

(37) J. Meinwald and N. J. Hudak, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 738.

in acetic acid. Samples were withdrawn at suitable intervals by a syringe and the chromium(VI) content of the sample was determined spectrophotometrically at 350 mμ.

b. Liquid Olefins. The measurements were carried out spectrophotometrically in a cell connected to an inverted U tube. The solution of the olefin in acetic acid and an appropriate amount of sulfuric acid in acetic acid was placed in one arm, a solution of chromic acid in the other. The system was degassed by evacuation using an oil pump and liquid nitrogen bath. After thermostating the arms to 25 ± 0.1° the reaction was started by mixing thoroughly the contents of the two arms, turning the cell assembly upside down, inserting the cell into a thermostated cell holder of a Zeiss PMQ II spectrophotometer, and following the rate of the reaction spectrophotometrically at 350 mμ. The final mixed volume was 5 ml.

Oxidation of the solvent containing sulfuric acid was small. However, all rate constants are corrected for solvent oxidation. The corrections ranged from 2 to 7%.

The concentrations of chromic acid in all kinetic runs was about 5×10^{-4} *M* except for *cis*-stilbene where it was 2.27×10^{-3} *M* (kinetic runs were carried out at 440 mμ, an alternative maximum for chromium(VI)). A 20-fold excess of the liquid olefin substrates were normally used; however, runs with about 200-fold excess were also carried out in the case of slower reacting olefins. Good straight-line plots of log *A vs.* time were obtained generally for about two half-lives and were used for the determination of the first-order rate constants. The second-order rate constants were calculated from initial olefin concentration. The values in the Table I are averages from at least 2 to 15 kinetic runs for each olefin.

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Solvolytic Displacement Reactions in Trifluoroacetic Acid. II. Trifluoroacetolysis of 1-Phenyl-2-propyl *p*-Toluenesulfonate

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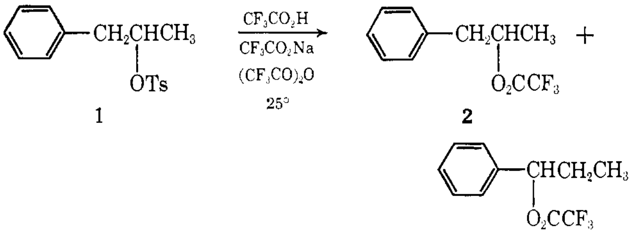
Abstract: The trifluoroacetolysis of 1-phenyl-2-propyl tosylate takes place with complete retention of configuration and in the presence of 20% excess sodium trifluoroacetate at 25.0° proceeds 17.1 times as fast as that of 2-propyl tosylate. Consideration of the phenyl group inductive effect leads to a rate enhancement factor for phenyl participation of 564 in this reaction.

Trifluoroacetic acid, by virtue of its powerful ionizing ability but weak nucleophilicity, provides a medium for solvolytic displacement reactions of particularly pronounced S_N1 character.[1–5] This medium offers anions highly efficient solvation through hydrogen bonding, but possesses correspondingly poor solvating properties toward cations. As a consequence, inductive and anchimeric assistance effects play enhanced roles in carbonium ion generation in trifluoroacetic acid[1–4] relative to the more nucleophilic solvents commonly employed.

We have recently reported a case of strongly amplified phenyl-group participation in this medium. The trifluoroacetolysis of 2-phenylethyl tosylate[2] was found to proceed over 3000 times as fast as that of ethyl tosylate, whereas the former substrate reacts more slowly than the latter in ethanol and acetic acid and only slightly faster in formic acid. The formation of 2-phenylethyl trifluoroacetate was shown to be accompanied by complete methylene-position interconversion,[2] and Jablonski and Snyder have subsequently demonstrated by stereospecific deuterium labeling that the reaction occurs with total retention of configuration.[3]

The powerful propensity for a β-phenyl group to assist ionization in a poorly nucleophilic medium was emphasized by preliminary results[2] on the buffered trifluoroacetolysis of 1-phenyl-2-propyl tosylate (**1**). This reaction took place smoothly at 25° to produce 1-phenyl-2-propyl trifluoroacetate (**2**) in 89% isolated yield, containing a trace of the hydride-shift product 1-phenyl-1-propyl trifluoroacetate (**3**), which polymerized slowly under the reaction conditions. Despite the presence of both an electronic and a steric bias against net phenyl migration in this carbonium ion system, the trifluoroacetolysis of tosylate **1** at 25° was found to be 20 times as fast as that of 2-propyl tosylate. The lat-



1

2

3 (trace)

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(2) J. E. Nordlander and W. G. Deadman, *ibid.*, 90, 1590 (1968).

(3) R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968).

(4) M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967).

(5) 2,2,2-Trifluoroethanol has recently been shown to exhibit similar properties as a solvolysis medium. See W. S. Trahanovsky and M. P. Doyle, *ibid.*, 2155 (1968).