

159–160°, m.m.p. 159–160°. *trans*-1,3-Cyclopentanediol^{7b} also was obtained from the cleavage mixture as the di-*p*-nitrobenzoate, m.p. 184–185°, reported⁷ m.p. 186° and the diurethan, m.p. 172–173°, reported⁷ m.p. 173°. Oxidation in anhydrous acetic acid gave *cis* and *trans*-3,4-diacetoxycyclopentene (37%), proven as before.

Oxidation in dry acetic acid with one equivalent⁴ of potassium acetate added gave 44% of a product shown later by periodic acid titration to be 97% *trans*-3,4-diacetoxycyclopentene, b.p. 85° at 1 mm. (*Anal.* Calcd. for $C_9H_{12}O_4$: C, 58.68; H, 6.57. Found: C, 58.85; H, 6.75), transformed similarly to *trans*-1,2-di-*p*-nitrobenzoxycyclopentane, m.p. 143–145°, m.m.p. 143–145°. In addition, a 3% yield of triester was obtained which was hydrolyzed to *trans*-3,4-cyclopentenediol and potassium glycolate.^{1a}

Reaction of lead tetrabenzoate and CPD^{1a}: in wet benzene gave a sufficient amount of benzoic acid and a non-crystalline *cis*-hydroxybenzoate (41%) transformed similarly to give *cis*-1-benzyloxy-2-*p*-nitrobenzoxycyclopentane (64%), m.p. 88–89° (*Anal.* Calcd. for $C_{19}H_{17}O_6N$: C, 64.23; H, 4.82; N, 3.94. Found: C, 64.13; H, 4.63; N, 3.91) and to give I, m.p. 116–118°, m.m.p. 116–118°.

In interpreting this, we invoke a Winstein neighboring cation,⁴ III, which opens *cis* with water (III → IV → VI) or carboxylic solvent (III → V → VII) and *trans* with carboxylate anion (III → VIII) utilizing the reactivity sequence, $H_2O > RCO_2^- > RCO_2H$.

In Criegee's experiments,¹ the stereochemistry of the 1,2-products was controlled by traces of water until consumed (III → IV → VI), then by carboxylic solvent (III → V → VII) until the effective anion concentration from divalent lead salts became dominant (III → VIII).

Utilizing Mosher's postulate,⁵ RCO_2^+ (II) or its equivalent, we account for the formation of III by attack⁸ of II on CPD and for glycolic ester formation by attack on the α -position of the diesters. Evidence of free radical attack was not found.^{1d,9}

An Armstrong Cork Co. Fellowship (F. J. V.) and a du Pont Co. Summer Faculty Fellowship (F.V.B., Jr.) are gratefully acknowledged.

(8) Other ionic paths are under consideration. The 3,5-by-products may arise from a 3,5-cation, similar to III.

(9) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951).

DEPARTMENT OF CHEMISTRY
HARRISON LABORATORY FREDERICK V. BRUTCHER, JR.
UNIVERSITY OF PENNSYLVANIA FULVIO J. VARA
PHILADELPHIA 4, PA.

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METHYL AFFINITIES OF ETHYLENE, TETRAFLUOROETHYLENE AND TETRACHLOROETHYLENE¹

Sir:

In the course of our studies of methyl affinities of aromatic and olefinic compounds we determined the relative rates of addition of methyl radicals to ethylene, tetrafluoroethylene and tetrachloroethylene. The results obtained demonstrate some fundamental principles governing the rate of radical addition reactions thereby deserving further discussion.

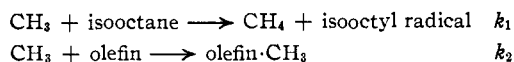
The methyl affinities are determined by a method described elsewhere,^{2,3,4} and represent the ratio k_2/k_1 .

(1) This work was supported by a grant from the National Science Foundation.

(2) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

(3) M. Levy and M. Szwarc, *THIS JOURNAL*, **77**, 2193 (1955).

(4) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **71**, 5493 (1955).



k_1 is a constant at constant temperature, while k_2 depends on the nature of the investigated olefin. Thus k_2/k_1 measures the relative rate of addition of methyl radicals.

Table I lists the obtained values (each an average of 4-10 experiments) of k_2/k_1 . The plots of $\log(k_2/k_1)$ against the reciprocals of temperature give excellent straight lines from which the following values for the activation energies $E_2 - E_1$ and temperature independent factors A_2/A_1 were obtained.

Ethylene	$E_2 - E_1 = -0.6$ kcal./mole	$A_2/A_1 = 13.0$
Tetrafluoroethylene	$E_2 - E_1 = -2.8$ kcal./mole	$A_2/A_1 = 5.3$

The reactivity of tetrachloroethylene is too low to determine the activation energy with any reasonable accuracy.

We conclude that the reactivity of tetrafluoroethylene is approximately ten times greater than that of ethylene, while tetrachloroethylene is unreactive. The higher reactivity of tetrafluoroethylene is shown to result from the lower activation energy of the addition reaction (as compared with ethylene), while the A_2/A_1 factor is lower for the reaction involving tetrafluoroethylene than that for ethylene. The methyl affinity of ethylene is comparable to that of vinylacetate, is approximately 80 times greater than that of benzene and $1/25$ as large as that of styrene.

TABLE I

Compound	T, °C.	k_2/k_1
Ethylene	54.7	37.3 ± 0.6
Ethylene	64.9	34.1 ± 2.2
Ethylene	74.8	34.6 ± 0.6
Ethylene	85.2	35.5 ± 1.5
Tetrafluoroethylene	54.7	400 ± 7
Tetrafluoroethylene	64.9	342 ± 14
Tetrafluoroethylene	74.8	307 ± 8
Tetrafluoroethylene	85.2	273 ± 8
Tetrachloroethylene	64.9	<0.3

The course of the addition of a radical to an aromatic or olefinic compound was discussed previously.^{1,2,3,5} It was pointed out that the transition state is determined by the crossing of the repulsion and attraction curves. The former represents an interaction between the "normal," non-excited molecule and the radical, and the latter shows an interaction between the excited molecule (say in its triplet state or an "electron localized" state) and the radical (see Fig. 1). The repulsion curve results probably from the coulombic force acting between the negative cloud of π electrons of the olefinic or aromatic compound and the negative cloud of the p electron of the approaching radical. If so, electron withdrawing groups should weaken the repulsion and flatten the repulsion curve (A in Fig. 1) while electron donating groups should strengthen the repulsion and make the curve steeper (C in Fig. 1). Hence, the activation energy of the addition process should decrease in the first case and increase in the second, this in turn increasing the methyl affinity in the former case and decreasing it in the latter. Such changes in the

(5) M. Szwarc, *J. Chem. Phys.*, **23**, 204 (1955).

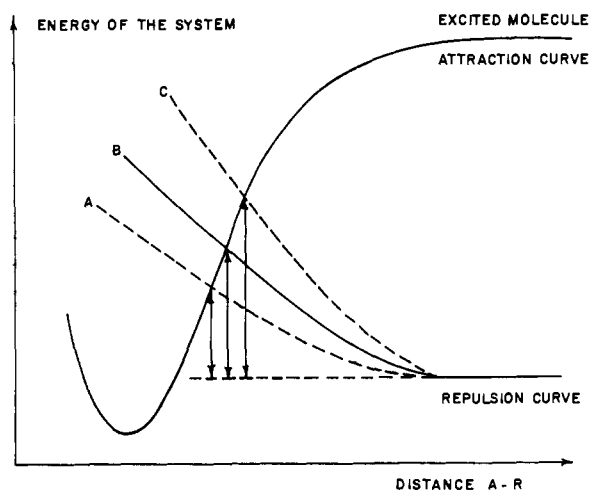


Fig. 1.

methyl affinities were observed in studies of reactions of substituted quinones.⁶ However, studies of methyl affinities of ethylene and tetrafluoroethylene show clearly that this effect is indeed due to a decrease in the activation energy of the process.

It was shown⁶ that the substitution of *all* the reacting positions by bulky chlorine atoms hinders the addition reaction (steric hindrance). This is observed also in the case of tetrachloroethylene. The difference in the behavior of small fluorine atoms and bulky chlorine atoms is spectacular.

(6) A. Rembaum and M. Szwarc, *This Journal*, **77**, 4468 (1955).

CHEMISTRY DEPARTMENT
STATE UNIV. OF NEW YORK
COLLEGE OF FORESTRY
SYRACUSE 10, N. Y.

R. P. BUCKLEY
M. SZWARC

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GAS PHASE IONIC REACTIONS. METHANE AND ETHYLENE

Sir:

We have measured rate constants and reaction cross sections for ionic reactions occurring in methane and ethylene in the ion source of a mass spectrometer. Recently Stevenson and Schissler¹ have reported similar measurements. A portion of our results is given in Table I. The rates depend upon the electric field strength in the mass spectrometer ionization chamber (*i.e.*, on the ion velocity), and the values given in the table are for a field strength of 10 v./cm. Table II shows a typical variation of the reaction rate constants and cross sections with field strength.

These constants and cross sections refer to exceedingly fast reactions. By way of comparison, the collision cross sections for methane and ethylene are² 12.3×10^{-16} cm.² and 17.1×10^{-16} cm.², respectively. Such very fast reactions will obviously be of importance in any process wherein ions are likely to be formed as, for example, in radiation chemistry processes. It is of interest, then, to at-

(1) D. P. Stevenson and D. P. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955); D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).

(2) Landolt-Börnstein, "Zahlenwerte und Funktionen," 6 Auflage, Atom- und Molekularphysik, 1 Teil, Springer Verlag, Berlin, 1950, p. 370.