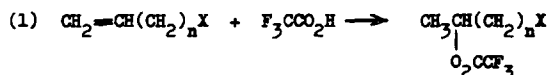


SLOW EXPONENTIAL DECREASE OF ALIPHATIC INDUCTIVE EFFECTS WITH
DISTANCE IN ADDITION OF TRIFLUOROACETIC ACID TO ALKENES
HAVING REMOTE SUBSTITUENTS¹

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(Received 17 July 1963)

AS an application of the recently reported enhanced inductive effect of certain substituents in trifluoroacetic acid², we have measured inductive rate depressions for the addition of trifluoroacetic acid to substituted alkenes having the substituent on the fourth, fifth, sixth, seventh and tenth carbon atoms from the potential secondary cationic carbon (equation 1).³ The magnitudes of the inductive rate



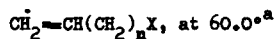
n = 3, 4, 5, 6, and 9

X = O₂CCF₃ and CN

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- 1 Presented in part at the Los Angeles meeting of the American Chemical Society, April, 1963; cf. Abstracts, Organic Division, p. 57M.
 - 2 a P. E. Peterson and G. Allen, *J. Org. Chem.*, **27**, 2290 (1962).
b The large magnitudes of the effect may be in part consequence of hydrogen bonding between trifluoroacetic acid and the substituent, as first proposed to explain fluorine nuclear magnetic resonance chemical shifts of meta substituted fluorobenzenes in trifluoroacetic acid; R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963).
 - 3 The potential cationic carbon, which could bear a substituent, is counted as number one.

depressions are appropriately measured by the quantity $\log k_n^H - \log k_n^X$ ($\Delta \log k$)_n^X where k_n^X and k_n^H are the first order rate constants (reported in Table I) for the reaction of the substituted and unsubstituted compounds, respectively, both of which have n methylene groups (cf, equation 1).⁴

Table I
Rates of Addition of Trifluoroacetic
Acid to Substituted Alkenes



n	$k \times 10^6, \text{ sec}^{-1}$		
	X = H	X = CN	X = O ₂ CCF ₃
3	1140	5.33	7.30
4	1470	23.8	45.6
5	1540	110	166
6	1680	298	377
9	1590	983	1060

(a) For solutions 0.1 M in alkene and 0.125 M in sodium trifluoroacetate

An interesting feature of the observed inductive rate depressions is that the fall-off of the effect with distance is given to a considerable degree of accuracy by one of the several alternative

⁴ The quantities $\log k$ are proportional to the free energies of activation by the definition of the latter; therefore, $\Delta \log k$ is proportional to the additional free energy of activation associated with the inductive substituent.

relationships which have been proposed in the literature for substituents closer to the reaction center, but which might be expected to fail in the case of more remote substituents. The relationship obeyed is the simple one involving the decrease of the inductive effect by a constant factor per methylene group separating the substituent and the reaction center, as given by equation 2. According

$$(2) (\Delta \log k)_{n+\alpha}^X = (\Delta \log k)_n^X (\epsilon)^\alpha$$

n = number of methylene groups separating the substituent and the reaction center for reference compounds having the closest substituent

α = number of additional methylene groups separating the substituent and the reaction center for compounds being compared with the reference compounds

ϵ = fall-off factor per additional methylene group

to this equation the inductive effect falls off as an exponential function of the number of intervening methylene groups. Taking logarithms of both sides gives equation 3. Since only $\log(\Delta \log k)_{n+\alpha}^X$

$$(3) \log(\Delta \log k)_{n+\alpha}^X = (\log \epsilon)(\alpha) + \log(\Delta \log k)_n^X$$

and α are assumed to vary for a series of compounds having the same substituent at various distances, (3) represents the equation of a straight line of slope $(\log \epsilon)$. The plot of our experimental data according to equation 3 is shown in Fig. 1.

The rates for both the cyanoalkenes and the trifluoroacetoxyalkenes lead to straight lines from the slopes of which ϵ values of 0.663 and 0.656, respectively, were calculated by the method of least squares. (The deviation of the point for hexenenitrile, for which $\alpha = 0$, is possibly associated with participation of the nitrile group in a cyclization reaction.) These ϵ values correspond to a surprisingly

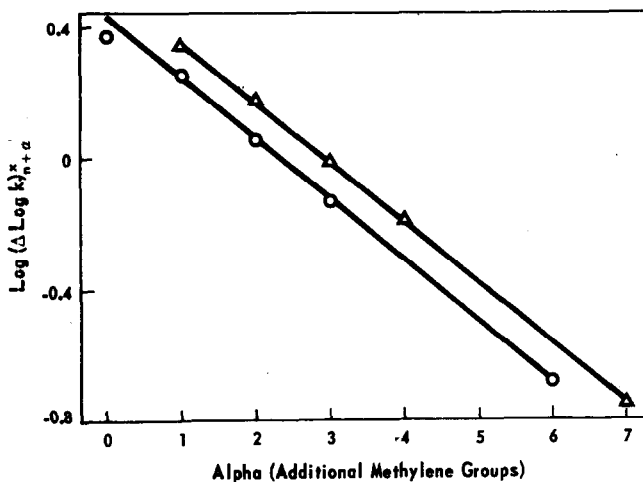
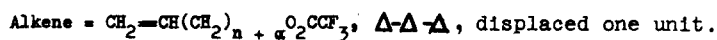
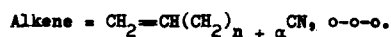


Fig. 1. Plot of rate data according to equation (3).



slow fall off of the substituent effect with distance, in view of the fact that values of 0.3 to 0.5 are usually found.⁵ In terms of equation 3, it is the combination of large ϵ values and the presumed solvent-enhancement of the inductive effect of the substituents which leads to the novel observation of significant rate effects due to substituents as far removed as ten carbon atoms from the reaction center.

5 J. C. McGowan, *J. App. Chem.*, 10, 312 (1960).