The Range of the Inductive Effect in Free-radical Substitution Reactions

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WE have recently argued on the basis of a large number of gas-phase chlorinations and brominations that no substituent in an aliphatic carbon chain effects the rate of attack by a halogen atom beyond the β-carbon atom.[1] These conclusions, based on our own gas-phase work, were at variance with reports by other workers who studied halogenation in the liquid phase.[2] We have now confirmed our own gas-phase results, but found that in acetonitrile solution substituents do indeed have a larger range effect. The gas-phase reactions were performed in a static system at *ca.* 20 mm. pressure.

TABLE 1.

Gas-phase Chlorination of Carboxylic Acid Derivatives: RS_4^x values at 60°

$COF{\cdot}CH_2$	CH_2	CH_2	CH_3		
0·02	0·37	1	0·24		
$COF{\cdot}CH_2$	CH_2	CH_2	CH_2	CH_3	
0·04	0·37	1	1·1	0·25	
$COF{\cdot}CH_2$	CH_2	CH_2	CH_2	CH_2	CH_3
0·05	0·4	1	1·0	1·1	0·25

TABLE 2.

Liquid-phase Chlorination of Carboxylic Acid Derivatives in Acetonitrile at 52°

$COCl{\cdot}CH_2$	CH_2	CH_2	CH_3		
0·06	0·40	1	0·44		
$COCl{\cdot}CH_2$	CH_2	CH_2	CH_2	CH_3	
0·09	0·32	1	1·4	0·62	
$COCl{\cdot}CH_2$	CH_2	CH_2	CH_2	CH_2	CH_3
0·06	0·50	1	1·3	1·5	1·1

The liquid-phase reactions were performed in acetonitrile solution (*ca.* 1 mole of acid chloride and 8 moles of acetonitrile). Analyses were by gas chromatography in a Griffin and George D6 apparatus in which the detector is a gas-density balance; it was assumed that the detector would have the same response for all isomers. The

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[1] H. Singh and J. M. Tedder, *J.*, 1964, 4737.

[2] H. J. Den Heitog and P. Smit, *Rec. Trav. chim.*, 1958, **77**, 73; C. Walling and M. F. Mayahi, *J. Amer. Chem. Soc.*, 1959, **81**, 1485.

results tabulated are a selection of a series of runs over a range of temperatures (each set of figures represents the mean of five or more runs at that temperature). The gas-phase results form an extremely consistent set. The results are quoted relative to the rate of attack at carbon atom 4. The almost identical RS values for the terminal methyl groups completely confirms our suggestion that the directive influence of the carbonyl group is not felt beyond the β-carbon atom. It is also of interest that the rate of attack at carbon atom 5 in hexanoyl fluoride and at carbon atom 6 in heptanoyl fluoride is slightly greater than that at carbon atom 4 as we have previously predicted.[3] At first sight the solution-phase results are completely irregular. It has long been known that in non-complexing solvents chlorination is less selective than in the gas phase (*e.g.*, for n-hexane $RS_2^1 = 2{\cdot}2$ at 49° in solution and $RS_2^1 = 3{\cdot}1$ at 50° in the gas phase[4]). However, the striking feature of the present results is that the rate of attack on the terminal methyl group increases as the chain is lengthened, in sharp contrast to the gas-phase results. This must mean that the deactivating influence of the carbonyl group is being felt well beyond the β-carbon atom, in accord with the suggestions of other workers using "non-complexing" solvents.[2] At first sight a solvent of high dielectric constant would be expected to decrease the importance of any direct field inductive effect (and atom to atom polarisation down the chain must be the same in the gas and liquid phase). The difference is clearly due to the solvation of the activated complex and of the products, so that in solution much greater separation of charge occurs. Although the interaction between this dipole and the dipole of the carbonyl group will be reduced by the presence of the solvent of high dielectric constant, this must be more than off set by the more polar nature of the activated complex and products in solution.

(*Received, November* 18*th*, 1964.)

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[3] P. S. Fredrick and J. M. Tedder, *Chem. and Ind.*, 1959, 490.

[4] I. Galiba and J. M. Tedder, unpublished work.