Comments on the Reactivity of Methoxy Pentadecyl Phenyl Isocyanate Isomers

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Synopsis

The reactions of 2-methoxy-4-pentadecyl phenyl isocyanate and 4-methoxy-2-pentadecyl phenyl isocyanate with excess 2-ethyl hexanol originally reported by Ghatge and co-workers to follow zero order kinetics have been re-examined on the basis of their data and shown to follow more realistically the product catalyzed pseudo first order kinetics. The new rate constants, k_s (sec^{-1}) for the spontaneous reaction and k_p (li. mole^{-1} sec^{-1}) for the product catalyzed reaction are found to be: $k_s = 0.57 \times 10^{-6}$ and $k_p = 34 \times 10^{-6}$ for 2-methoxy-4-pentadecyl phenyl isocyanate and $k_s = 1.2 \times 10^{-6}$ and $k_p = 82 \times 10^{-6}$ for 4-methoxy-2-pentadecyl phenyl isocyanate.

INTRODUCTION

A recent publication by Ghatge and co-workers[1] described the synthesis and reactivity of the two isomeric isocyanates, 2-methoxy-4-pentadecyl phenyl isocyanate(I) and 4-methoxy-2-pentadecyl phenyl isocyanate(II) with 2-ethyl hexanol.
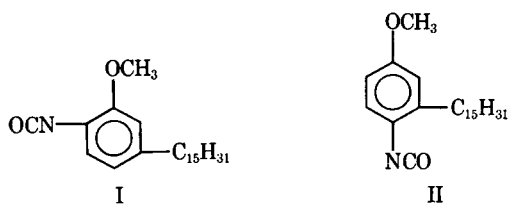
The kinetics of the reaction in benzene were studied by infrared spectroscopy following a method originally developed by Bailey and co-workers.[2] The disappearance of the isocyanate was monitored by recording the change in absorbance of the strong carbonyl stretching band of the isocyanato group at 2270 cm^{-1}. Since the reactions were conducted in the presence of a tenfold excess of the alcohol the results should have fitted pseudo first order kinetics quite closely. However, the authors have interpreted their results as following zero order kinetics.

This being a drastic departure from all previous studies on the reactivity of isocyanates with alcohols it seemed pertinent to re-examine their data and check the validity of their interpretation.

Discussion

The mechanism and kinetics of the reaction of isocyanates with alcohols have been thoroughly investigated by a number of investigators.[3-15] The subject has been of sufficient commercial and theoretical importance to have stimulated the appearance of excellent reviews.[16,17]

In its details the reaction mechanism of isocyanates with alcohols is quite complex. According to Sato,[12] in both the spontaneous (noncatalyzed) and the catalyzed reactions, third order kinetics are observed for which the following general expression applies.

$$\frac{dx}{dt} = k_1(a - x)(b - x)^2 + k_2 x(a - x)(b - x) + k_3(\text{cat})\ (a - x) \times$$

$$(b - x) \quad (1)$$

The first term in the right-hand side of eq. (1) accounts for the fact that the reactant alcohol itself catalyzes the reaction. The second term takes into account the catalytic effect of the product urethane, while the last term applies to the special cases where a catalyst is used to accelerate the reaction.

For the reactions examined in the present study where a large excess of alcohol was used and no additional catalyst was employed, the rate expression is simplified as shown below.

$$\frac{dx}{dt} = k_s(a - x) + k_p(x)(a - x) \quad (2)$$

k_s = rate constant for the spontaneous pseudo first order reaction
k_p = product catalyzed rate constant

Following common procedures solution of eq. (2) is accomplished as follows.

$$\frac{dx}{(a - x)\ (k_s + (x)k_p)} = dt \quad (3)$$

Applying the technique of partial fractions.

$$\frac{1}{(a - x)\ (k_s + (x)k_p)} = \frac{A}{a - x} + \frac{B}{k_s + (x)k_p} \quad (4)$$

one obtains

$$A = \frac{1}{k_s + ak_p} \quad B = \frac{k_p}{k_s + ak_p} \quad (5)$$

$$\frac{dx}{(k_s + ak_p)\ (a - x)} + \frac{k_p dx}{(k_s + ak_p)\ (k_s + xk_p)} = dt \quad (6)$$

Upon integration the solution is found to be

$$\frac{2.303}{k_s + ak_p} \log \frac{a\ (k_s + xk_p)}{k_s(a - x)} = t \quad (7)$$
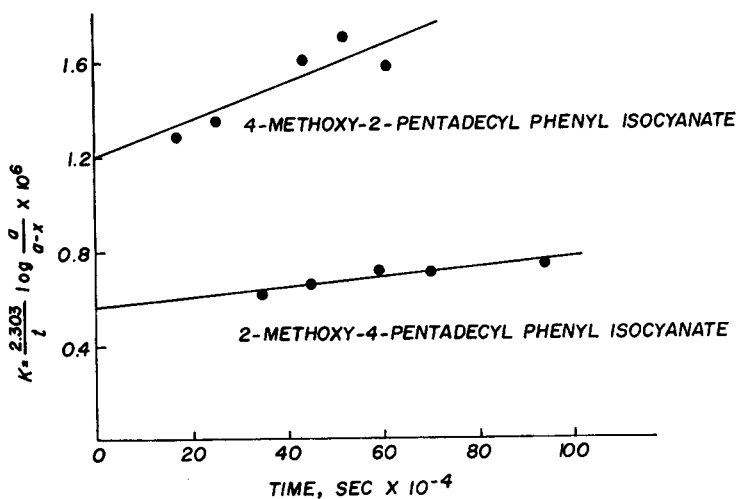
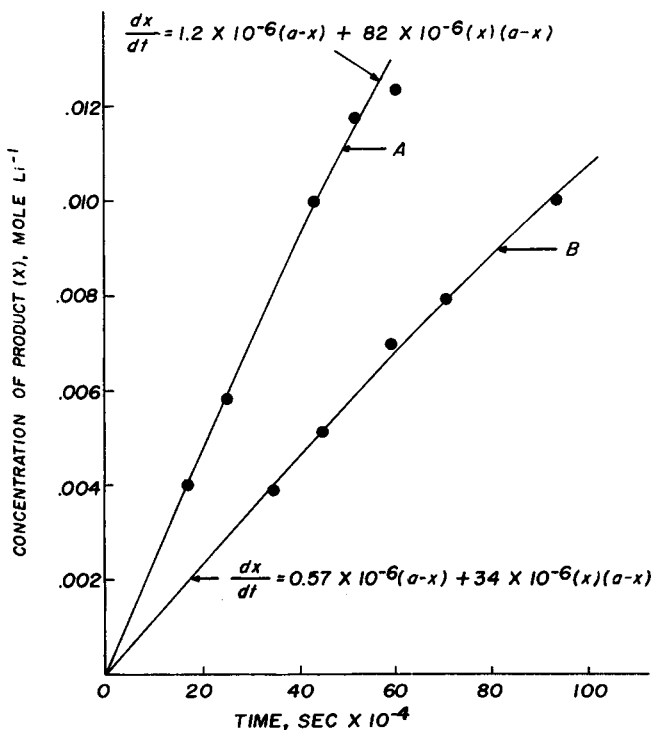Fig. 1. Variation of first order rate constants with time.

Fig. 2. Experimental points and calculated curves for the reaction of 3-methoxy-2-pentadecyl phenyl isocyanate (curve A), and 2-methoxy-4-pentadecyl phenyl isocyanate (curve B).

The value of the rate constant k_s for the spontaneous reaction was estimated by applying the pseudo first order rate treatment to Ghatge's data using eq. (8) below, plotting the k_s values obtained as a function of time and extrapolating the least square line to zero as shown in Figure 1.

$$k_s = \frac{2.303}{t} \log \frac{a}{a - x} \tag{8}$$

By this procedure the value estimated for the spontaneous rate constant rounded off to only two significant figures is 0.57×10^{-6} sec^{-1} for 2-methoxy-4-pentadecyl phenyl isocyanate and 1.2×10^{-6} sec^{-1} for 4-methoxy-2-pentadecyl phenyl isocyanate.

With these values for k_s and upon inserting on a trial and error basis different values of k_p into eq. (7), curves were constructed which reproduced the experimental data of Ghatge very closely as shown in Figure 2. The values of k_s and k_p for both isocyanates are given in Table I.

TABLE I
Rate Constant Calculations for the Isocyanates Reaction with 2-Ethyl Hexanol

Reactant	k_s, sec^{-1}	k_p, li. mole^{-1} sec^{-1}
2-methoxy-4-pentadecyl phenyl isocyanate	0.57×10^{-6}	34×10^{-6}
4-methoxy-2-pentadecyl phenyl isocyanate	1.2×10^{-6}	82×10^{-6}

Conclusion

On the basis of the foregoing treatment it is submitted that the data for the two aromatic isocyanates fit more realistically the product catalyzed pseudo first order expression than the zero order expression suggested by Ghatge and co-workers.

References

1. N. D. Ghatge, S. D. Yadav, and A. C. Ranade, *J. Appl. Polym. Sci.*, **12**, 447–453 (1968).
2. M. E. Bailey, V. Kirss, and R. G. Spaunburgh, *Ind. Eng. Chem.*, **48**, 794 (1956).
3. T. L. Davis and J. M. Farnum, *Jrl. Am. Chem. Soc.*, **56**, 883 (1934).
4. J. W. Baker and J. B. Holdsworth, *Jrl. Chem. Soc.*, 713 (1947).
5. J. W. Baker, M. M. Davies, and J. Gaunt, *J. Chem. Soc.*, 24 (1949).
6. J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 9 (1949).
7. J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 19 (1949).
8. J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 27 (1949).
9. M. Morton and M. A. Deisz, paper No. 34, presented at the Amer. Chem. Soc. Meeting, Atlantic City, Sept. 1956.
10. J. Burkus and C. F. Eckert, *J. Am. Chem. Soc.*, **80**, 5948 (1958).
11. A. Farkas and K. G. Flynn, *J. Am. Chem. Soc.*, **82**, 642 (1960).
12. Masao Sato, *J. Am. Chem. Soc.*, **82**, 3893 (1960).
13. Yoshio Iwakura, Hisao Okada, and Seiichi Yamashiro, *Die Makromolekulare Chemie*, **58**, 237 (1962).

14. Hisao Okada and Yosnio Iwakura, *Die Makromol. Chem.*, **66**, 91 (1963).

15. K. G. Flynn and D. R. Nenortas, *J. Org. Chem.*, **28** (12), 3527 (1963).

16. J. H. Saunders and K. C. Frisch, *Polyurethanes*, Interscience, New York, 1962.

17. A. Farkas and G. A. Mills, *Catalytic Effects in Isocyanate Reactions*, Advances in Catalysis, Vol. 13, Academic Press Inc. New York, 1962.