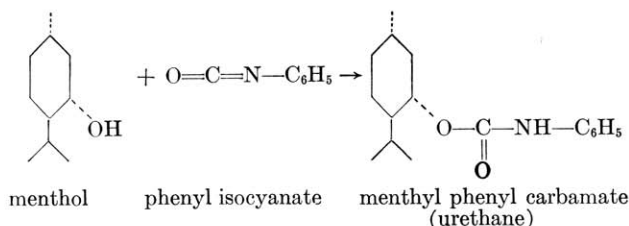


# Infrared Spectrometry To Study Second Order Reaction Kinetics

Infrared spectroscopy is well known as a useful method for the qualitative determination of functional groups. By contrast, quantitative infrared spectrometry does not appear to have such a good reputation. Although this latter method is rapid and simple, it has a number of small drawbacks: unprecise base line to the peaks, presence of small or broad interfering bands, absorption by the solvent, inconstant cell temperature, lack of electronic stability of the spectrometer with time and imperfect proportional response of the pen. However, the main difficulties are deviations from the Beer-Lambert law and the comparatively large width of the slits in relation to the thickness of the absorption band.

Advantages and defects of infrared quantitative determinations have been summarized briefly in classical reference works, and more completely in some review articles (1, 2). Integrated intensities have been studied intensively (3-6). Infrared spectrometry has been applied to the kinetics of reactions (7, 8). This paper describes a laboratory experiment used in the Faculté des Sciences, Paris, for an undergraduate course in "Chimie Organique Structurale."

The reaction chosen is



The kinetics are studied by the increase in intensity of the C=O band at 1730 cm<sup>-1</sup> with time.

The following preliminary experiments could be performed by the students: using the same cells and solvent (carbon tetrachloride) as for the kinetics determination, the Beer-Lambert law is shown to be valid for small concentrations (0-0.045 M) of phenyl urethane. The transparency of carbon tetrachloride is checked at 1730 cm<sup>-1</sup> using a fixed cell (0.2 mm) and a variable path cell; a 50% increase in thickness of the latter, from the compensation point, is shown not to displace the base line. Diphenyl urea, the usual impurity of phenyl isocyanate, gives no band in the 1730 cm<sup>-1</sup> region (Nujol). However, we have found that menthol (9-11) has a slight continuous absorption at this wavelength and that phenyl isocyanate (9, 12-16) gives a small band at 1723 cm<sup>-1</sup>. These facts must not be neglected and adequate corrections are therefore introduced.

The equation giving the absorption as a function of time can be deduced as follows: the sealed sample cell

(Fig. 1) is supposed to be formed by two windows with vacuum in between. The solvent *s*, the menthol *m*, the phenyl isocyanate *i*, and the phenyl urethane *u* are supposed to be situated in separate layers having the same thickness *L* as the cell. The symbols employed here are the following: *A'*, absorbance of the

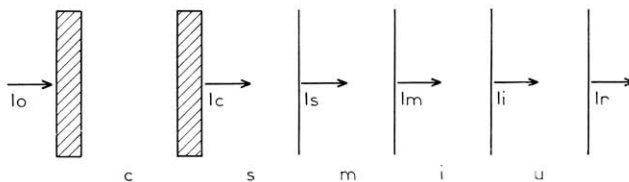


Figure 1.

empty cell;  $\epsilon_s$ ,  $\epsilon_m$ ,  $\epsilon_i$ ,  $\epsilon_u$ , molecular extinction coefficients of the various compounds;  $c_s$ ,  $c_m$ , ..., concentrations (*M*) at time *t* (min);  $I_0$ ,  $I_r$ ,  $I_c$ , ..., initial, residual, and various intensities. Then,

$$\log(I_0/I_c) = A'$$

$$\log(I_c/I_s) = \epsilon_s c_s L \dots$$

$$A = \log(I_0/I_r) = L(\epsilon_m c_m + \epsilon_i c_i + \epsilon_u c_u) + A''$$

where *A''* is a constant equal to the total absorbance of the cell and of the solvent. Using equimolar proportions of menthol and phenyl isocyanate at *c*<sub>0</sub> initial concentrations:

$$c_m = c_i = c_0 - c_u$$

$$A = L(\epsilon_u - \epsilon_m - \epsilon_i)c_u + A''' \quad (1)$$

where

$$A''' = L(\epsilon_m + \epsilon_i)c_0 + A''$$

*A'''* is the absorbance of the menthol and phenyl isocyanate at time zero plus the absorbance of the cell and solvent. The equation (1) expresses the fact that the absorbance *A* at 1730 cm<sup>-1</sup> increases with time and is proportional to the concentration of phenyl urethane.

If the reaction is of the second order:

$$\begin{aligned} dc_u/dt &= kc_m c_i = k(c_0 - c_u)^2 \\ (c_0^2/c_u) - c_0 &= 1/kt \end{aligned} \quad (2)$$

Replacing *c<sub>u</sub>* by the value given by (1):

$$\frac{1}{A - A'''} = \frac{1}{c_0^2 L(\epsilon_u - \epsilon_m - \epsilon_i)k} \cdot \frac{1}{t} + \frac{1}{c_0 L(\epsilon_u - \epsilon_m - \epsilon_i)} \quad (3)$$

This last equation shows that in the case of a second order reaction, 1/(*A* - *A'''*) must be proportional to 1/*t*.

The experimental results obtained with an Infracord 137B or a Perkin-Elmer 221 spectrometer are found to agree with a second order rate as expected. The kinetics of the formation of urethanes has been studied by several authors (8, 18-22) and shown to correspond to an autocatalytic or base-catalyzed reaction with an initial second order rate and with formation of intermediate adducts.

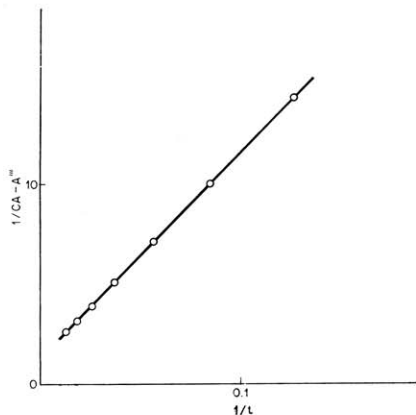


Figure 2. Linearity of  $1/(A-A'')$  versus  $1/t$  demonstration second-order kinetics for urethane formation.

The apparatus is checked as usual and the results are recorded on the customary sheet of paper with logarithmic ruling. Two 0.2-mm NaCl sealed cells are filled with carbon tetrachloride and the base line is placed at the optical density of 0.02. Thereafter the reference cell is left in place and the adjustment knobs are not touched.

First,  $A''$  is determined. This symbol represents, in the case of a double beam apparatus, the sum of the absorbances at  $1730\text{ cm}^{-1}$  of menthol and of phenyl isocyanate at time zero with the base line as origin. These two values are obtained by filling the sample cell successively with 0.3 M solutions of menthol and then of phenyl isocyanate with the following results:

$A'' = 0.031$  (Infracord) and  $0.029$  (Perkin-Elmer 221)

The kinetics of the reaction are studied by preparing separately 0.6 M carbon tetrachloride solutions of 1-menthol and of phenyl isocyanate, mixing them (time zero), and filling the sample cell quickly. The spectrophotometer is run in a cyclic manner during approximately 90 min, for as long as the Beer-Lambert law remains valid. It is easy to check that  $1/(A-A'')$  is proportional to  $1/t$  (Infracord, Fig. 2). Therefore the reaction is of the second order.

#### Literature Cited

- (1) PHILPOTTS, A. R., AND MADDAMS, W. F., *Proc. Intern. Symposium Microchem.*, Birmingham Univ., 1958, 373; *Bibl. Chem. Rev.*, **3**, 69b (1960).
- (2) LECOMTE, J., *Bull. Soc. chim. France*, 1959, 1080.
- (3) JONES, R. N., AUGDAHL, E., NICKON, A., ROBERTS, G., AND WHITTINGHAM, D. J., *Ann. N. Y. Acad. Sci.*, **69**, 38 (1957).
- (4) MILLS, I. M., *Ann. Rept. Progr. Chem.*, **55**, 55 (1958).
- (5) BROWN, T. L., *Chem. Rev.*, **58**, 581 (1958).
- (6) ARNAUD, P., *Bull. Soc. chim. France*, 1961, 1037.
- (7) HOUGHTON, R. P., PhD Thesis, London, 1958.
- (8) KOGON, I. C., *J. Org. Chem.*, **24**, 438 (1959).
- (9) BARNES, R. B., LIDDEL, U., AND WILLIAMS, V. Z., *Ind. Eng. Chem., Anal. Ed.*, **15**, 684, 694 (1943).
- (10) BARNES, R. B., GORE, R. C., LIDDEL, U., AND WILLIAMS, V. Z., "Infrared Spectroscopy. Industrial Applications and Bibliography," Reinhold Pub. Co., New York, 1944, p. 61.
- (11) NAVES, Y.-R., AND LECOMTE, J., *Bull. Soc. chim. France*, 1955, 792.
- (12) EYSTER, E. H., AND GILLETTE, R. H., *J. Chem. Phys.*, **8**, 369 (1940).
- (13) THIEBAUT, R., *Ann. chim. (Paris)*, [12] **8**, 72 (1953).
- (14) HOYER, H., *Ber. deut. chem. Ges.*, **89**, 2677 (1956).
- (15) CALDOW, G. L., AND THOMPSON, H. W., *Spectrochim. Acta*, **13**, 212 (1958).
- (16) NAKANISHI, KOJI, "Infrared Absorption Spectroscopy," Holden Day Ind., San Francisco, 1962, p. 131.
- (17) DAVID, D. J., *Anal. Chem.*, **35**, 37 (1963).
- (18) SAUNDERS, J. H., AND SLOCOMBE, R. J., *Chem. Rev.*, **43**, 203 (1948).
- (19) ARNOLD, R. G., NELSON, J. A., AND VERBANC, J. J., *Chem. Rev.*, **57**, 47 (1957).
- (20) EPHRAIM, S., WOODWARD, A. E., AND MESROBIAN, R. B., *J. Am. Chem. Soc.*, **80**, 1326 (1958).
- (21) SATO, M., *J. Am. Chem. Soc.*, **82**, 3893 (1960).
- (22) LOVERING, E. G., AND LAIDLER, K. J., *Can. J. Chem.*, **40**, 31 (1962).