The kinetics of the reaction of isophorone di-isocyanate with mono-alcohols

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Isophorone di-isocyanate (IPDI) is used to react with hydroxyl containing prepolymers in the preparation of polyurethane elastomers, particularly with hydroxy-terminated polybutadiene (HTPB) in composite propellant systems. In the present work, the kinetics of the reaction of IPDI with monoalcohols are studied, as a model for the polyurethane systems. A gas chromatography method is used to follow the reaction, which allows direct measurement of the reaction of individual isocyanate groups. The rates of individual isocyanate groups are described by a second order equation modified to include catalysis by the urethane products. The rates of primary and secondary isocyanate groups in the two isomers of IPDI are compared. Differences between the various isocyanate groups are relatively small, and are offset by the urethane catalysis effect, so that the overall disappearance of isocyanate is roughly second order. The reaction rate of IPDI with HTPB is faster than with the model compounds, and it is suggested that this arises because there is tendency for the isocyanate to complex with the hydroxyl end groups of the polymer.

(Keywords: kinetics; isophorone di-isocyanate; mono-alcohols; prepolymers; polyurethane elastomers; hydroxy-terminated polybutadiene)

INTRODUCTION

Isophorone di-isocyanate (IPDI) has been adopted as the curing agent for hydroxy terminated polybutadiene (R45M or R45HT) in a number of propellant binder systems[3]. Clearly, the details of the cure reaction, particularly as regards completeness of the reactions and the presence of side reactions, are of importance to the properties of the final propellants. The present investigations were initiated as part of a programme to investigate the ageing of these systems.

The most common methods of studying the cure kinetics of di-isocyanates[1,2] are infra-red spectroscopy and chemical measurement of the residual isocyanate groups. Both these measurements measure only the total isocyanate content. Consideration of the structure of IPDI, structure I, shows that more detailed information is desirable.

I
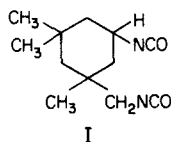
As written in structure I, there are clearly two types of isocyanate groups in the molecule, a primary one, CH_2–NCO, and a secondary one, CH–NCO. Moreover, it has been shown by n.m.r. spectroscopy and gas chromatography that the molecule consists of a mixture of two isomers, IIa and IIb, according to whether the NCO and CH_2NCO are cis or trans to each other on the cyclohexane ring. Estimates of the isomer ratio from ^1H and ^{13}C n.m.r. and gas chromatography indicate similar values of about 72% of the cis isomer and 28% of the trans isomer.

IIa (trans)

IIb (cis)
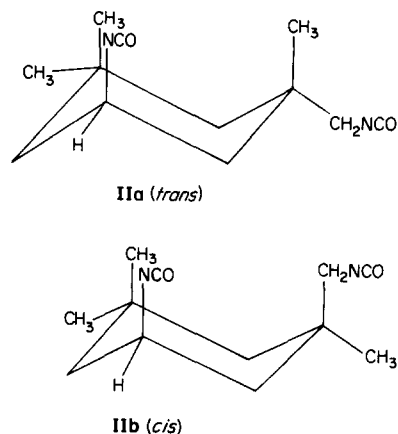
Thus, IPDI contains 4 different types of isocyanate groups. Moreover, as for any di-isocyanate, there is the possibility of the reactivity of one group depending on whether the other group is isocyanate or has reacted to form a urethane group. Thus, the reaction kinetics are potentially very complicated. It has been suggested that there is a substantial difference in reactivity between the different groups, which would be important in ensuring that the cure reaction goes to completion.

In addition to these considerations, the reaction kinetics of a single isocyanate group are complicated. Although the reaction is approximately second order[1], it is generally accepted that more complex equations are necessary, and a variety of equations have been used, involving uncatalysed terms and catalysis by alcohol and urethane as well as added catalysts such as tertiary amines. By using gas chromatography, supported by n.m.r. spectroscopy, to study the reaction of IPDI with small molecule mono-alcohols, these features can be

studied in more detail. The objective of the present work was therefore to investigate the reaction of IPDI with alcohols with regard to the kinetic equations necessary to describe the reaction of individual groups and the relative reactivities of the different isocyanate groups.

KINETIC EQUATIONS

A number of equations have been suggested to describe the kinetics of the reaction of an isocyanate with an alcohol. In a classic series of papers Baker and co-workers[4-6] studied the catalysed and uncatalysed reaction of phenyl isocyanate with simple alcohols. These results were described in terms of a general base catalysed reaction.

$$RNCO + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [RNCO:B] \xrightarrow[R'OH]{k_3} RNHCOOR' \qquad (1)$$
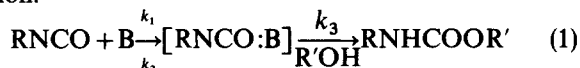
Assuming a stationary state condition, in the absence of an uncatalysed reaction, this leads to the rate equation:

$$\frac{-d(RNCO)}{dt} = \frac{k_1 k_3 (RNCO)(R'OH)(B)}{[k_2 + k_3(R'OH)]} \qquad (2)$$

For the alcohol catalysed reaction, the base B is R'OH, and equation (2) gives:

$$\frac{-d(RNCO)}{dt} = k_1 k_3 (RNCO)(R'OH) \left[\frac{(R'OH)}{k_2 + k_3(R'OH)} \right] \qquad (2a)$$

This general reaction scheme is frequently employed for the reaction of aromatic isocyanates with alcohols. However, for aliphatic isocyanates, Sato[7] has suggested an equation of the form:

$$\frac{dx}{dt} = k_1(a-x)(b-x)^2 + k_2(x)(a-x)(b-x)$$
$$+ k_3(cat)(a-x)(b-x) \qquad (3)$$

where x, $a-x$ and $b-x$ are the concentrations of urethane, isocyanate and alcohol respectively, and the 3rd term applies to the case of added catalyst. It appears that the second term in equation (3), corresponding to urethane catalysis, is more important for aliphatic isocyanates than for aromatic ones.

In a slightly different approach Anxuino et al.[8] attributed the deviation from second order kinetics to the formation of allophanate
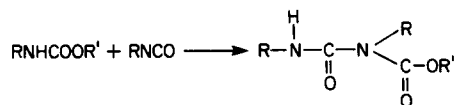
This will give equations which are similar to, but different from, those obtained when catalysis by urethane occurs. They applied the same equations to both aliphatic and aromatic isocyanates, and interpreted the extent of deviation from second order as a measure of the amount of allophonate formation. They point out that the rate and order of reaction is very dependent on the solvent used, and assumed that the catalytic effect of the urethane group could be neglected in the dipolar solvent, dimethyl-acetamide, which they used.

Although these approaches appear to be very different, it is easily shown that for appropriate values of the rate

constants, they can give quite similar behaviour corresponding to approximately second order kinetics, and a large number of papers have shown that the reaction of a single isocyanate group with an alcohol is approximately second order, with various amounts of deviation depending on the system[1]. In the case of di-isocyanates, particularly those with two different isocyanate groups, it is frequently assumed that the reaction of each group is second order, so that deviation from second order kinetics is interpreted in terms of different reactivities of the two groups. In many cases, different reactivities of the two isocyanates may be a very important factor in the deviation of the overall disappearance of isocyanate groups with time. However, in view of the complexities of the reaction of a single isocyanate group, it is necessary to be very cautious in interpreting deviations in the disappearance of total isocyanate with time to specific causes, be they the difference in rate constants for different groups or the formation of allophonate groups. In order to measure the reactivity of different isocyanate groups it is desirable to have a method of measuring the concentrations of the individual groups, as in the present study.

In the present case, ^1H and ^{13}C n.m.r. and g.l.c. did not show the presence of allophonate groups in the model systems, so that the approach of Anzuino et al[8] was not adopted. The equation of Sato[7] (equation (3)) was found to give a reasonable description of the equimolar reactions. However, it will be seen that it does not give a good description of reactions in which the initial alcohol concentration is varied over a considerable range. This deficiency is understandable when the equation is considered more carefully. In the absence of added catalyst, Sato's equation takes the form:

$$\frac{dx}{dt} = k_1(a-x)(b-x)^2 + k_2 x(a-x)(b-x) \qquad (4)$$

This may be written:

$$\frac{dx}{dt} = (a-x)(b-x)\{k_1(b-x) + k_2 x\}$$
$$= (a-x)(b-x)\{k_1 b + (k_2 - k_1)x\} \qquad (5)$$

For much of the data described by Sato's equation, $k_2 > k_1$. It is clear that equation (5) has the same form as a 2nd order equation with an additional term for urethane catalysis, *for constant initial alcohol concentration b*. The 3rd order nature of the alcohol catalysis term only becomes apparent when the initial alcohol concentration is varied. Sato's equation is very often applied to data in which constant, equimolar alcohol and isocyanate concentrations are employed. Under these conditions, a 3rd order alcohol catalysis term with rate constant k_1 is indistinguishable from a 2nd order term with rate constant $k_1 b$. We found that our data for equimolar reactants could be fitted reasonably with equation (4). However, when the alcohol concentration was increased by a factor of ten, the 3rd order equation gave very inaccurate values for the reaction rates. In fact, the initial rates, in which the urethane catalysis term is zero, are fitted well by a second order equation.
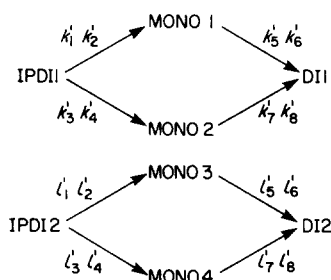
We therefore suggest that, rather than Sato's equation, the empirical equation (6) should be used. Results pre-

sented in this paper, particularly the variation of initial rates on varying the alcohol concentration, show that this equation gives a better description of the IPDI/alcohol system.

$$\frac{dx}{dt} = k_1 \cdot (a-x)(b-x) + k_2 \cdot (a-x)(b-x)x \qquad (6)$$

The equations of Baker and co-workers[4-6] can include urethane catalysis by incorporating two terms with the form of equation (2), with base B corresponding to alcohol and urethane respectively. Equation (6) can be derived from this with appropriate values of k_1, k_2 and k_3 and suitable approximations. In the present work, because of the complexity due to isomerism and different types of isocyanate groups, equation (6) represents a suitable, relatively simple equation to use.

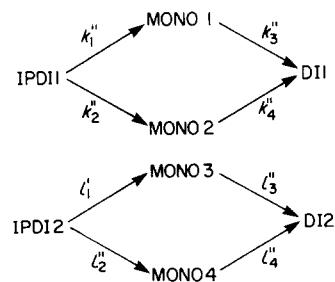*IPDI/alcohol system as a series of parallel and consecutive reactions*

IPDI1 — k_1', k_2' → MONO 1 — k_5', k_6' → DI1
IPDI1 — k_3', k_4' → MONO 2 — k_7', k_8' → DI1

IPDI2 — l_1', l_2' → MONO 3 — l_5', l_6' → DI2
IPDI2 — l_3', l_4' → MONO 4 — l_7', l_8' → DI2

The above reaction scheme represents the reaction of IPDI, consisting of two isomers 1 and 2, with a mono-alcohol. The pairs of rate constants (k_3', k_4'), (l_2', l_2') etc. correspond to the rate constants k_1 and k_2 for the second order and urethane catalysed terms respectively in equation (6). Mono-urethanes 1 and 2, for example, are produced by reactions of IPDI1 with either the primary or secondary isocyanate group. In principle, this leads to a large number of rate constants. Some of these will only be different if it is assumed that the reaction of one isocyanate group is dependent on the form of the other group. For example, k_1' and k_2' are the same as k_7' and k_8' if the reaction of one isocyanate group is the same for the other group being either an isocyanate or a urethane group. However, the data required different values for these constants. In order to simplify the equations as much as possible, we have attempted to reduce the number of rate constants as much as possible. This can be achieved by slightly altering equation (6) to give:

$$\frac{dx}{dt} = k_1''(a-x)(b-x)\{1 + k_2'''x\} \qquad (7)$$

We assume that, as an approximation, we can use the same value of k_2''', the ratio of the urethane catalysis term to that for alcohol catalysis, for all reactions. Any variation in rate constants for the different isocyanate groups arises only from variation in k_1'. Thus, the overall reaction scheme is described in terms of one rate constant k_2''' and 8 rate constants for reaction of the individual isocyanate groups.

This gives rise to a series of coupled differential equations. No attempt was made to obtain algebraic solutions to these equations, since no approximation such as the steady state one is valid. With the use of a digital

IPDI1 — k_1'' → MONO 1 — k_3'' → DI1
IPDI1 — k_2'' → MONO 2 — k_4'' → DI1

IPDI2 — l_1'' → MONO 3 — l_3'' → DI2
IPDI2 — l_2'' → MONO 4 — l_4'' → DI2

computer, calculation of the concentration of the various species as a function of time can be readily accomplished in a simple way, without any approximations whatsoever.

The program calculates the reaction profile in the simplest and most straightforward way possible, by dividing the reaction into a series of equal time increments, calculating the incremental change in concentration of each of the reactants in this time increment, and adding the change to each reactant species. The process is then repeated for each time increment to give the concentration of species at a series of finite times. Thus, the increment in the concentration of monourethane 1 in a time interval Δt is given by:

$$\Delta(MONO1) = [k_1''(IPDI1)(alcohol)\{1 + k_2''(urethane)\}$$
$$- k_3''(MONO1)(alcohol)$$
$$\{1 + k_2''(urethane)\}]\Delta t$$
$$(MONO1(t + \Delta t)) = (MONO1(t)) + \Delta(MONO1)$$

Provided that the time interval Δt is made sufficiently small, this approach can be used to calculate the reaction profile to any degree of accuracy. The smaller Δt, however, the greater the computing time required, and the value of Δt was chosen to give accuracy of the order of 0.1% with a reasonable amount of computation. The approach was checked by using the method to calculate a second order rate reaction, which could be checked against the algebraic solution, and, by using rate constants similar to those necessary for the system of interest, time increments of 300 and 30 s were found to be adequate for equimolar and tenfold alcohol excess reactions respectively.

EXPERIMENTAL

Reagents

IPDI was obtained from Scholven Chemie AG. It was purified by distillation before use. Alcohols were purified by distillation and stored over magnesium sulphate to dry them. The heptane and carbon tetrachloride reaction solvents were dried over sodium wire.

Reactions

Reactions were carried out in glass ampoules sealed under vacuum. In addition to the IPDI, alcohol and heptane solvent, approximately 0.3 g of cicosane was added as an internal marker for gas chromatography. After an appropriate reaction time, an ampoule was removed from the bath, and the contents were dissolved in a five-fold excess of tetrahydrofuran (THF), since it was found that for the longer reaction times there was a tendency for a solid product to separate out from the heptane solutions on cooling to room temperature. An aliquot of the THF solution was then injected onto a Perkin Elmer F17 gas chromatograph.

Gas chromatography

Gas chromatographs were obtained on a Perkin Elmer F17 gas chromatograph, equipped with a 4 metre × 3 mm i.d. glass column packed with 3% OV 101 on 80–100 mesh Chromasorb WHP. The column temperature was programmed from 170°C to 270°C at 5°C/min. The injector and flame ionization detector were maintained at 275°C. The carrier gas was nitrogen at a flow rate of 33 ml min^{-1}. 1 μl aliquots of the reaction solutions diluted five-fold in THF were injected. The relative areas of IPDI and its derivatives and the cicosane internal marker were measured on a Spectra-Physics Autolab IVB computing integrator.

N.m.r. spectroscopy

From the same stock solutions as used for gas chromatography, samples were placed in 5 mm and 10 mm n.m.r. tubes for ^{1}H and ^{13}C n.m.r. respectively. Between measurements the samples were kept in an oil bath at 60°C, and measurements were carried out with the spectrometer probe set at a nominal temperature of 60°C. ^{1}H measurements were made using a Jeol PS-100 n.m.r. spectrometer in the field sweep continuous wave mode. ^{13}C measurements were made using the PFT-100 accessory in the pulsed Fourier Transformer mode. From the correlation between n.m.r. and g.l.c. results, it was possible to assign the g.l.c. peaks to IPDI1 and IPDI2, the monourethanes and the diurethanes. It was only possible to resolve the 4 monourethanes into 3 peaks, the two monourethanes from IPDI1 being unresolved.

RESULTS

Ideally, it would be of interest to study the reaction kinetics with a range of different alcohols, varying the concentration of reactants and reaction temperature over a wide range. However, in view of the limited effort which could be devoted to the study, conditions were chosen to be as close as possible to the polybutadiene/IPDI propellant binder system. Initial studies were carried out with isopropanol, but allyl alcohol was considered to be the best model available for hydroxy-terminated polybutadiene. Normal heptane was chosen as a suitable solvent. The reaction temperature of 60°C and the approximately equimolar concentrations of IPDI and alcohol were the same as those normally employed in the propellant system.

The isopropanol/IPDI system was investigated with the intention of defining the most suitable kinetic equations. Firstly, we considered the initial reaction rates for an approximately equimolar reaction and one with 8.4 times excess of isopropanol. The disappearance of IPDI for the excess isopropanol case showed a first order dependence on isocyanate concentration. By considering the initial reaction rates, any dependence on urethane catalysis is eliminated. Thus, the initial reaction rates for equation (6), for equation 2(a) of Baker and co-workers,

equation (4) of Sato should show respectively a first order, intermediate order between 1 and 2, and second order dependence on alcohol concentrations. By considering the initial rates, we may calculate rate constants for equimolar and excess alcohol reactions on the basis of equations (4) and (6). The results are shown in *Table 1*.

It is seen that the data fits exceptionally well for the second order rate equation (first order in isocyanate and alcohol), suggesting that equation (6) is the correct one for this isocyanate. Surprisingly, the data do not show any additional dependence on alcohol concentration beyond this simple second order equation, in contrast to the results of Baker and coworkers[4–6] for aromatic isocyanates.

Having adequately described the initial rates, we next attempted to fit the total reaction profile for the stoichiometric reaction. The first calculations used a series of simple second order equation, as required for the initial rates, equating the urethane catalysis rate constant k_2'' in equation (7) to zero. While this gave an adequate description of the early stages of the reaction it was found that in the later stages the calculated values showed increasing deviation from the observed ones. It was apparent that the reaction did not slow down to the expected extent as the concentration of alcohol and isocyanate decreased. This effect can be corrected by the urethane catalysis term in equation (7); that is, by a non-zero value of k_2'' in equation (7). In principal, this introduces a large number of rate constants, since there are a pair of rate constants for each individual reaction. However, by assuming that the urethane catalysis is proportionally the same for each of the individual reactions, we greatly reduce the number of adjustable parameters. Thus, we use the same value of k_2'' in equation (7) for all the isocyanate reactions, and thus have a single parameter for urethane catalysis.

With this assumption it was possible to fit the details of the kinetics for the stoichiometric reaction between IPDI and isopropanol at 60°C. The results are shown in *Figure 1*, with the parameters given in *Table 2*. While the fit is not perfect, it is clear that the calculations describe the reaction profiles in a satisfactory way. The rate constants show that the differences in reactivity between different isocyanate groups in IPDI are relatively small, the largest variations being about a factor of 2.5 times.

A better model alcohol for the hydroxy terminated polybutadiene (HTPB) used in propellants is allyl alcohol, since the HTPB end groups are primary allylic ones. The approximately stoichiometric reaction at 60°C was therefore carried out for this alcohol. Again, a reasonable fit of the reaction profile could be achieved with the model. Typical data are shown in *Figure 2*, with the parameters given in *Table 2*. In fact, the rate constants obtained are similar to those for the isopropanol system. This result is somewhat unexpected, as it is usually found that primary alcohols are appreciably more reactive than secondary ones[1,4–6].

Table 1 Rate constants for 2nd and 3rd order dependence for initial rates

Total isocyanate concentration (mol litre^{-1})	Alcohol concentration (mol litre^{-1})	Rate constant k_1' according to equation (6) (litres mol^{-1} s^{-1})	Rate constant k_1 according to equation (4) (litres^2 mol^{-2} s^{-1})
0.6308	0.7081	2.21 × 10^{-5}	3.11 × 10^{-5}
0.4672	3.9300	2.20 × 10^{-5}	5.60 × 10^{-6}

Table 2 Rate constants for the reaction of IPDI with mono-alcohols treated as a series of consecutive reactions

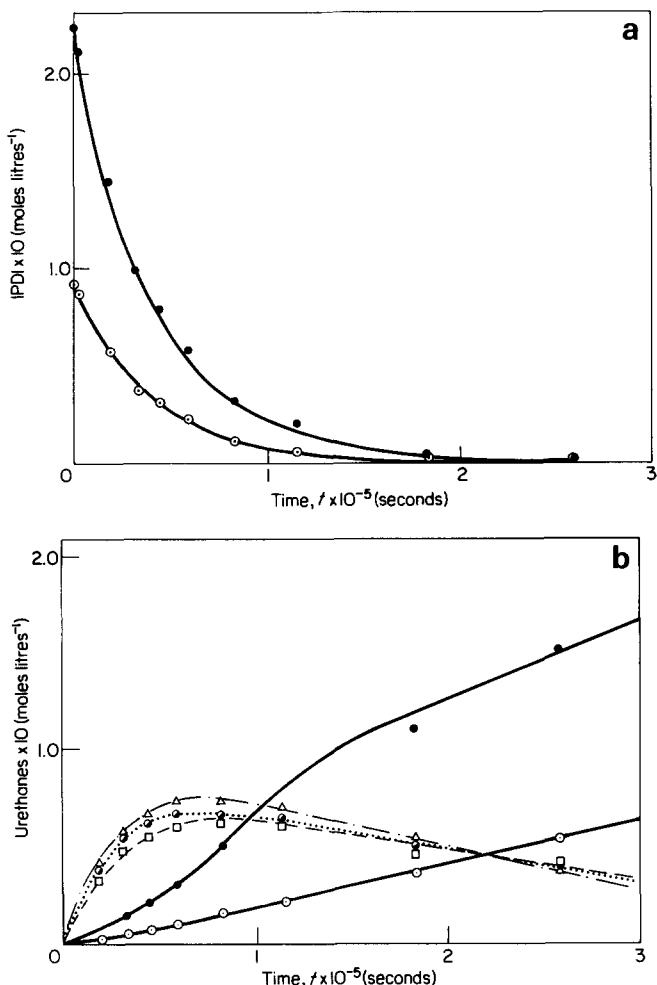| Alcohol	Rate constants x 10^5 (litres mol^{-1} s^{-2})								
	k_1''	k_2''	k_3''	k_4''	l_1''	l_2''	l_3''	l_4''	k_2'''
Isopropanol	2.3	2.3	1.5	1.5	2.3	2.0	1.0	1.8	2.5
Allyl alcohol	2.3	2.3	0.9	0.9	2.5	2.5	1.3	1.2	2.5

Figure 1 Calculated (——) and observed (○) reaction profiles for the stoichiometric reaction of IPDI and isopropanol at 60°C. (a) Disappearance of IPDI 1 (○) and IPDI 2 (●) (b) Appearance and disappearance of monourethanes 1 and 2 (---□---), monourethane 3 (...◑...) and monourethane 4 (---△---), and appearance of diurethane 1 (—○—) and diurethane 2 (——●——)

In all the data given in *Table 2*, it is clear that there is not a great variation between the rate constants for different isocyanate groups in the IPDI system. Thus the maximum variation between the fastest and slowest rate constant is approximately 2.5. Moreover, because of the form of the rate equation describing the data, the overall effect is even less marked. This is because of the marked urethane catalysis of the reaction. For a single isocyanate group, this would have the effect of speeding up the reaction towards the end, in comparison with a second order reaction. In the present complicated system, this urethane catalysis tends to compensate for the more slowly reacting isocyanate groups, so that the system approximates to a fairly constant second order rate. This is illustrated in *Figure 3*, which shows the disappearance of total iso-cyanate plotted as a second order plot for the equimolar

IPDI/allyl alcohol reaction. The data fits fairly well for a single second order reaction.

The rate constants obtained from the model compound studies seem to be appreciably lower than those for the R45M/IPDI system measured by infra-red spectroscopy, contrary to our expectation of slower rates in the more viscous polymer system. To check that this did not indicate experimental errors in one or other of the methods, identical IPDI/allyl alcohol systems were studied by g.l.c. and infra-red. Because of the different forms of the rate equations used, the data is best compared by plotting the disappearance of total isocyanate with time in both cases, as in *Figure 3*. The infra-red data for allyl alcohol was appreciably slower than the R45M reaction, and, as shown in *Figure 3*, the agreement between the g.l.c.
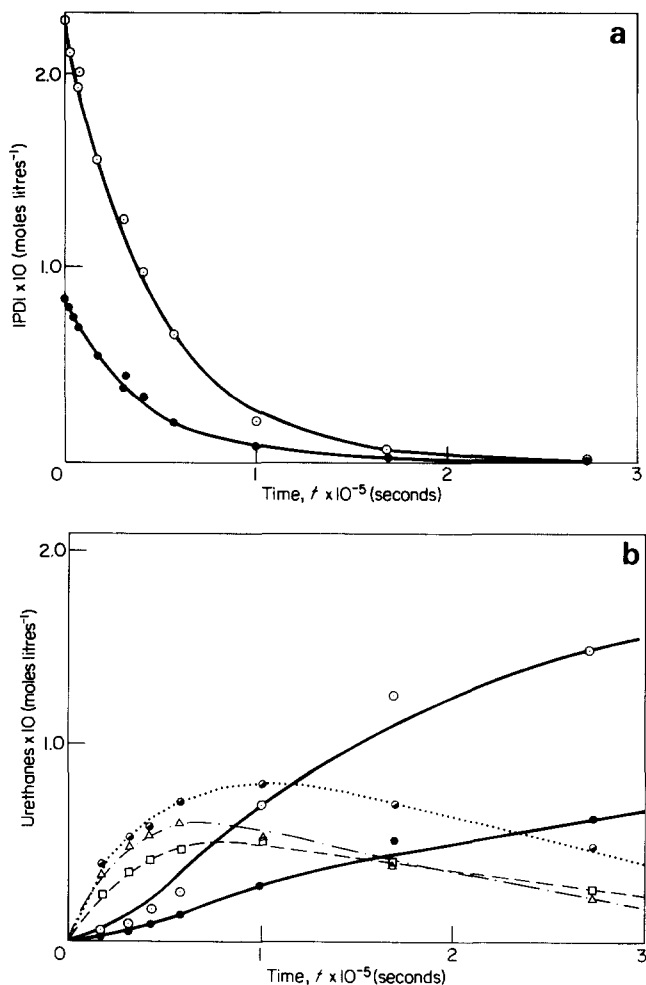
Figure 2 Calculated (——) and observed (○) reaction profiles for the stoichiometric reaction of IPDI and alkyl alcohol at 60°C. (a) Disappearance of IPDI 1 (X) and IPDI 2 (○). (b) Appearance and disappearance of monourethanes 1 and 2 (——□——), monourethane 3 (·· ◑ ··) and monourethane 4 (·· -△-·), and appearance of diurethane 1 (—X—) and diurethane 2 (—○—)
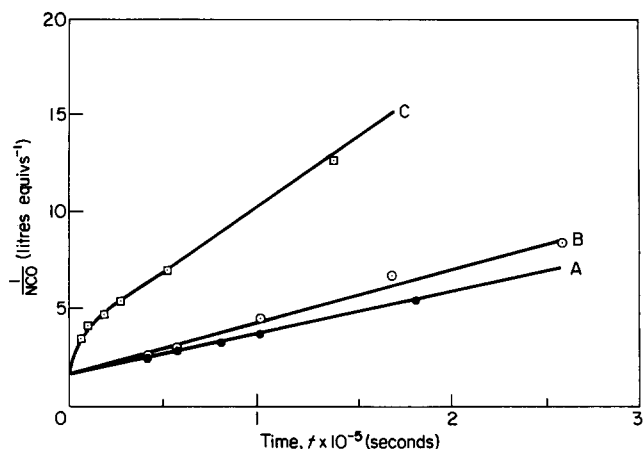
Figure 3 2nd order plot of the disappearance of total isocyanate. (A) IPDI/allyl alcohol, g.l.c. data (—X—); (B) IPDI/allyl alcohol, infra-red data (— ⊙ —); (C) IPDI/R45M HTPB, infra-red data (—⊡—)

and infra-red runs is acceptable. The i.r. run is still slightly faster. The largest difference appears to be due to a fast initial reaction, which appears to be characteristic of the polymer reaction but is not observed in the g.l.c. data. The results do indicate that the difference between the R45M/IPDI reactions studied by i.r. and allyl alcohol/IPDI g.l.c. runs is mainly due to the different diol, the polymer reaction being faster than the model compound. This may be explained in terms of a tendency of the IPDI to complex with the alcohol groups, the tendency being greater in the polymer system than in the model compound, although other explanations, such as the presence of catalyst residues in the polymer, are possible.

CONCLUSIONS

The reaction of the di-isocyanate IPDI with mono-alcohols, a model for the cure of rubbery propellant binders, has been studied by g.l.c. The method allows the rate constants for the four individual isocyanate groups to be measured separately. The kinetics of each group are adequately described by a second order rate equation, modified to include a term for catalysis by the urethane product. The rate constants for the individual groups are more similar than had previously been suggested, the fastest and slowest rate constant differing only by a factor of 2.5. Moreover, the effect of the slowest rate constant is compensated by an increase in rate due to urethane catalysis. Thus, a reasonable approximation to the overall cure rate is given by a simple second order equation. Similar rate constants were obtained for isopropanol and allyl alcohol. It was found that the overall rate constants for the model alcohols were lower than that for the R45M hydroxy-terminated polybutadiene prepolymer used in propellant systems. The model systems did not show a high initial rate characteristic of the polymer reaction. It is suggested that this effect arises because of a tendency for IPDI to complex with the HTPB chain ends at high concentrations.

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