Studies in the Reactivities of Isocyanates*

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Synopsis

Disubstituted monoisocyanates were synthesized and their reactivities studied by the spectroscopic method.

In recent times polyurethane polymers have become commercially important, and information on the reactivities of the different isocyanates needed for different purposes is also becoming important.

Reaction rates of phenyl isocyanates with 1- and 2-butanol have been reported by Dyer et al.[1] Substituent effects on the reactivities of aryl monoisocyanates have been reported by Bailey et al.[2] Similarly, reactivities of isocyanates in terms of the Hammett equation have been reported by Kaplan.[3]

The present paper describes the syntheses of isocyanates with the use of an indigenously available raw material and the determination of the reactivities of the monoisocyanates with 2-ethyl hexanol by the simple spectroscopic method.
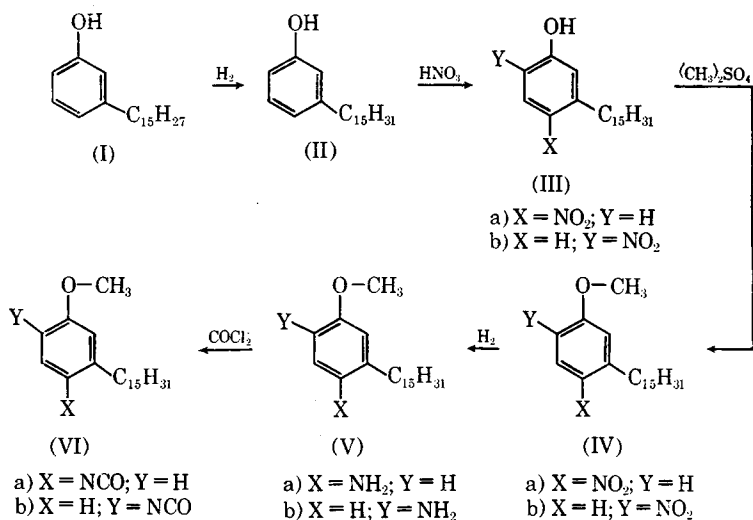
Cashew nut shell liquid (CNSL), which is indigenously available, has been utilized for various applications in the paint, plastics, and rubber industries.[4] The main constituent in the commercially available CNSL is a monohydric *meta*-substituted alkenyl phenol. This phenol has been utilized in the preparation of substituted monoisocyanates of lesser reactivities, which may find some use in coatings for paper, textile, and leather and in adhesives.

The methods that have been utilized for the syntheses of these isocyanates are shown diagrammatically on the next page.

INSTRUMENT

The spectra were recorded on a Perkin-Elmer Model 221 spectrophotometer equipped with a sodium chloride prism. The instrument was previously calibrated with standard polystyrene film. All measurements were made at room temperature (24 ± 1°C.) with the same pair of cells (0.02 mm. in thickness).

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\text{(I)} \xrightarrow{H_2} \text{(II)} \xrightarrow{HNO_3} \text{(III)} \xrightarrow{(CH_3)_2SO_4}
$$

(I) — OH, $C_{15}H_{27}$

(II) — OH, $C_{15}H_{31}$

(III) — OH, Y, X, $C_{15}H_{31}$

a) X = NO$_2$; Y = H
b) X = H; Y = NO$_2$

(VI) $\xleftarrow{COCl_2}$ (V) $\xleftarrow{H_2}$ (IV)

(VI) — O—CH$_3$, Y, X, $C_{15}H_{31}$

a) X = NCO; Y = H
b) X = H; Y = NCO

(V) — O—CH$_3$, Y, X, $C_{15}H_{31}$

a) X = NH$_2$; Y = H
b) X = H; Y = NH$_2$

(IV) — O—CH$_3$, Y, X, $C_{15}H_{31}$

a) X = NO$_2$; Y = H
b) X = H; Y = NO$_2$

EXPERIMENTAL

3-Pentadecyl Phenol (II)

Commercial cashew nut shell liquid, when distilled under reduced pressure, gave 3-alkenyl phenol (anacardol), b.p. 195–200°C. at 2 mm. (60%). The anacardol was then catalytically reduced to 3-pentadecyl phenol (tetrahydroanacardol) over nickel catalyst at 600 lb. hydrogen pressure and 60°C. temperature. Crystallization from petroleum ether (40–60°C.) yielded a soft white mass, m.p. 49–50° (80%).

4-Nitro-3-pentadecyl Phenol (IIIa) and
6-Nitro-3-pentadecyl Phenol (IIIb)

Tetrahydroanacardol, on nitration with fuming nitric acid (sp. gr. 1.5), gave the mixed mononitro isomers. The method for nitration was the same as that adopted by Dawson and Wasserman,[5] and the yields were similar to that reported.

4-Nitro-3-pentadecyl Anisole (IVa) and
6-Nitro-3-pentadecyl Anisole (IVb)

These compounds were obtained by methylating the respective nitrophenols with dimethyl sulfate by the method of Dawson.

4-Amino-3-pentadecyl Anisole (Va)

4-nitro-3-pentadecyl anisole (5 g.) dissolved in absolute alcohol (125 cm.³) was taken in a round-bottomed flask, and Raney nickel (1 g.) was then added to it. Hydrazine hydrate (80%, 2.6 cm.³) was then added dropwise with proper shaking. The mixture was then refluxed on a water bath for 2 hr. It was then filtered hot and, on concentration of the filtrate, crystals

separated. On recrystallization from ethanol the compound melted at 44.5° (66%).

ANAL. Found: C, 79.52%; H, 11.71%. Calcd. for $C_{22}H_{39}NO$: C, 79.29%; H, 11.71%.

The hydrochloride melted at 114–115°C.

6-Amino-3-pentadecyl anisole (Vb)

The same procedure as described for the preparation of 4-amino-3-pentadecyl phenol was followed. The compound melted at 67.5°C. (65%); Dawson reports m.p. 67.5°C.

4-Methoxy-2-pentadecyl Phenyl Isocyanate (VIa)

4-Amino-3-pentadecyl anisole hydrochloride (1 g.) dissolved in mono-chlorobenzene (30 cm.³) was taken in a three-necked 100 cm.³ flask fitted with N_2 inlet tube, stirrer, and condenser with an attachment tube leading to the exhaust. A toluene solution of phosgene (20 cm.³, 12.5%) was then added at 0°C., and the mixture was kept overnight. Next day the mixture was refluxed on a sand bath for 1 hr. Nitrogen was then bubbled through the mixture until no presence of phosgene was detected by the indicator paper. The mixture was filtered and chlorobenzene removed under reduced pressure. The residual gummy mass was distilled under reduced pressure, the product distilling at 240–250°C. at 0.3 mm. (80%) and a ν_{max} of 2270 cm.$^{-1}$.

ANAL. Found: C, 77.00%; H, 10.5%; N, 4.26%. Calcd. for $C_{23}H_{37}NO_2$: C, 76.98%; H, 10.3%; N, 3.89%.

Ethyl urethane had m.p. 74.5°C.

ANAL. Found: C, 74.89%; H, 10.48%. Calcd. for $C_{25}H_{43}NO_3$: C, 74.74%; H, 10.6%.

2-Methoxy-4-pentadecyl Phenyl Isocyanate (VIb)

The same procedure as that described above for the preparation of 4-methoxy-2-pentadecyl phenyl isocyanate was followed. The compound distilled at 240–250°C. at 0.3 mm. and on solidification melted at 39°C. (80%) and a ν_{max} of 2260 cm.$^{-1}$.

ANAL. Found: C, 79.4%; H, 10.27%; N, 3.89%. Calcd. for $C_{23}H_{37}NO_2$: C, 76.9%; H, 10.3%; N, 3.89%.

Ethyl urethane had m.p. 60°C.

ANAL. Found: C, 75.03%; H, 10.85%. Calcd. for $C_{25}H_{43}NO_3$: C, 74.74%; H, 10.61%.

METHOD OF DETERMINING REACTIVITY RATES OF ISOCYANATES

The intensity of the infrared absorption caused by an isocyanate group at ≈2270 cm.$^{-1}$ is employed for plotting the course of the reaction kinetics.
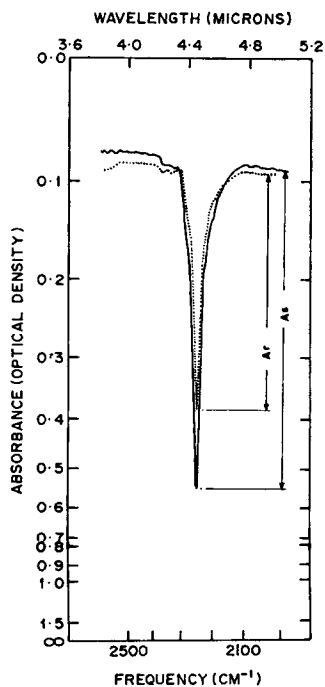
Fig. 1. Optical densities of the monoisocyanate and the reaction mixture of monoiso-
cyanate and 2-ethyl hexanol.

Two samples of the isocyanate in question are weighed in standard flasks. One of the samples is dissolved in benzene to give $0.02N$ solution, which is used as the standard, S. To the other flask 0.2 mole of 2-ethyl hexanol is added, and the mixture is made up to the calibration mark with benzene, to give the reaction mixture, R. After thorough shaking both solutions, standard S and the reaction mixture R are placed in the cells and the intensity of the infrared absorption band appearing at ≈2270 cm.$^{-1}$ is recorded. The absorbance A_R with respect to time for the two isocyanates, as recorded by the instrument, are shown in Tables I and II. The concentration of unreacted isocyanate is calculated according to the equation (Fig. 1) $C = A_t/A_s \times 0.02$, where A_t is the absorbance after the lapse of a given time and A_s is the absorbance at the start of the reaction.

TABLE I

Optical Density with Respect to Time of a Mixture of 2-Pentadecyl
4-Methoxy Phenyl Isocyanate and 2-Ethyl Hexanol at 24 ± 1°C.

	Time, hr.					
	0	48	71	121	145	169
Absorbance A_R	0.315	0.25	0.223	0.157	0.13	0.121
Unreacted iso- cyanate, %	100	80.00	70.79	49.84	41.27	38.41

TABLE II

Optical Density with Respect to Time of Mixture of 2-Methoxy-4-penta-
decyl Phenyl Isocyanate and 2-Ethyl Hexanol at 24 ± 1°C.

	Time, hr.					
	0	96	125	165	197	261
Absorbance A_R	0.478	0.38	0.355	0.312	0.289	0.238
Unreacted iso-cyanate, %	100	80.76	74.27	65.28	60.46	49.79

RESULTS

The observed chemical reaction fits well with the zero-order reaction kinetics given by the equation $K_t = A_s - A_t$, where A_s is the absorbance at the start of reaction and A_t is the absorbance after a lapse of time t.

Zero-order reaction rate constants for the two isocyanates were calculated for individual points in the experiments and averaged as shown in Tables III and IV.

TABLE III

Zero-Order Reaction-Rate Constant of 2-Pentadecyl-4-methoxyl
Phenyl Isocyanate

	Time, hr.				
	48	71	121	145	169
Rate constant, sec.$^{-1}$ ($\times 10^{-7}$)	3.761	3.599	3.627	3.544	3.188
Average rate constant, sec.$^{-1}$			3.544×10^{-7}		

TABLE IV

Zero-Order Reaction-Rate Constant of 2-Methoxy-4-pentadecyl
Phenyl Isocyanate

	Time, hr.				
	96	125	165	197	216
Rate constant, sec.$^{-1}$ ($\times 10^{-7}$)	2.835	2.727	2.795	2.727	2.525
Average rate constant, sec.$^{-1}$			2.772×10^{-7}		

DISCUSSION

Much information on the kinetics of the reaction of isocyanates with alcohols is available, and the reaction has been reported as a second-order reaction. Bailey et al. in the spectroscopic method employed for isocyanate kinetic studies had assumed an approximate first-order kinetics, because substantial excess of alcohol was used in his studies. In the present inves-
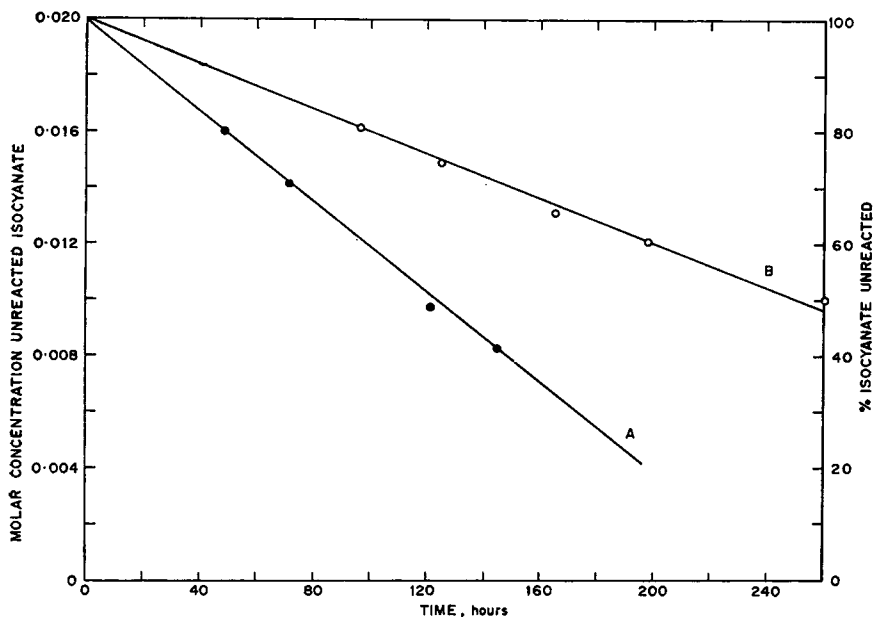
Fig. 2. Rates of reaction of the isocyanates (VIa) and (VIb) with 2-ethyl hexanol: (A) 2-pentadecyl-4-methoxy phenyl isocyanate; (B) 2-methoxy-4-pentadecyl phenyl isocyanate.

tigation the technique employed is essentially that of Bailey, but the reaction was observed to fit well with zero-order kinetics, as shown by the results in Tables III and IV and Figure 2.

It is shown by Bailey that substitution of a group such as NO_2 and Cl in the isocyanate molecule enhances the positive charge on the carbonyl carbon of the isocyanate group and, hence, the isocyanate molecule becomes more reactive. It is also shown that substitution of a group such as alkyl (CH_3) or alkoxyl (OCH_3) in the isocyanate molecule decreases the positive-ion concentration on the carbonyl carbon of the isocyanate group and, hence, the isocyanate molecule becomes less reactive. Kaplan has also reported the reactivities of many disubstituted monoisocyanates. Here also the same phenomena of reactivity associated with nitro, chloro, methyl, and methoxy groups have been reported.

In the present case in one instance the *para* and *ortho* positions in the isocyanate molecule are occupied by an alkoxyl and a long-chain alkyl group, respectively. In the other instance the *para* and *ortho* positions are occupied by a long-chain alkyl and an alkoxyl group, respectively. The influence of the two groups in the two instances are the same but, when they occupy reverse positions in the same isocyanate molecule, the combined influence of the two shows a vast difference in the reactivities.

Alkyl and alkoxyl groups, when they are present in the position *ortho* to an isocyanate group, reduce the reactivity of the isocyanate group, the

alkoxyl influencing more than the alkyl group. Similar observations are noted when the *para* position in the isocyanate molecule is occupied by these groups. The influence of the *ortho* substitution is more than the influence of the *para* substitution in the isocyanate molecule. This may be because in the *ortho* substitution the effect is electronic as well as steric. In the present study it is observed that the combined electronic and steric effects of the long-chain alkyl group in the *ortho* position and the electronic effect of the alkoxyl group in the *para* position of compound (VIa) is much less than the combined electronic and steric effects of the alkoxyl group in the *ortho* position and the electronic effect of the long-chain alkyl group in the *para* position of compound (VIb).

CONCLUSION

The technical importance of slowly reacting isocyanate is felt much more when we find that the isocyanate reactions in many cases get out of hand because of the high reactivity of the isocyanates. In another sense, these slowly reacting isocyanates could be used in place of the "blocked isocyanates" used in coatings for paper, textile, leather, and copper wire and in adhesives.

References

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