THERMOCHEMICAL STUDIES OF SOME ALCOHOL–ISOCYANATE REACTIONS

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ABSTRACT

The heats of reaction of normal-, iso-, and secondary-butyl alcohols reacting with phenyl isocyanate, the three tolyl isocyanates, and 2,4-tolylene diisocyanate were measured at 25° C, using a differential calorimeter of the Tian–Calvet type. The results are interpreted in terms of substituent effects.

From bond energy considerations the heats of formation of phenyl isocyanate and tolyl isocyanate have been estimated.

INTRODUCTION

Polyurethanes, formed by the reaction of a diisocyanate with a dihydroxy alcohol or polyol, are playing an increasingly important role in plastics technology. There is a lack of heat of reaction data for reactions of this type, and heats of formation for aryl isocyanates and urethanes do not appear to be available. In view of this situation it was decided to measure the heats of reaction of some simple alcohol–isocyanate reactions, since these are relevant to the more complicated reactions giving rise to polyurethanes. The reactions studied were those of normal-, iso-, and secondary-butyl alcohols with phenyl isocyanate, the three tolyl isocyanates, and 2,4-tolylene diisocyanate.

The only heats of formation available concerning isocyanates are those of Lemoult (1), who measured the heat of combustion of methyl and ethyl isocyanates. He reported the heat of combustion of liquid ethyl isocyanate to be 424.4 kcal mole^{-1}, but reported no analysis of the combustion products. Heats of formation do not appear to be available for any urethane of the type R—NH—COO—R′, although Kharasch (2) gives the heat of formation of urethane itself. The heat of formation of a few di-*N*-substituted urethanes are given by Schmidt (3). Recently Skinner and Snelson (4) have determined the heats of combustion of the four butyl alcohols at 25° C. The heats of formation of normal-, iso-, and secondary-butyl alcohols in the liquid state were given as -78.49 ± 0.20, -80.00 ± 0.20, and -81.88 ± 0.22 kcal mole^{-1} respectively.

EXPERIMENTAL

Purification and Preparation of Materials

The normal- and iso-butyl alcohols used were Fisher Certified Reagents. Secondary-butyl alcohol was a Fisher "Highest Purity" grade material. The alcohols were dried by refluxing over freshly ignited calcium oxide for 4 hours followed by fractionation through a 40-cm column packed with short lengths of 4-mm glass tubing. Only the middle fractions (collected at 117.7°, 108.4°, and 99.5° C for normal-, iso-, and secondary-butyl alcohols respectively) were retained. The alcohols were tested for dryness using the method suggested by Dyer, Taylor, Mason, and Samson (5). One or two drops of phenyl isocyanate were added to a sample of the alcohol; if no crystals of insoluble *sym*-diphenyl urea formed the alcohol was considered to be suitable for the experiments.

The phenyl and tolyl isocyanates used were manufactured by Eastman Organic Chemicals. They were purified by double vacuum distillation, the last distillation taking place immediately prior to use. Analysis of the distilled isocyanate using the Stagg technique (6) indicated that the isocyanates were between 99.5% and 100.5% pure. The boiling points and approximate boiling pressures for the isocyanates were phenyl: 46° C, 5 mm; *o*-tolyl: 57° C, 10 mm; *m*-tolyl: 62° C, 5 mm; *p*-tolyl: 66° C, 10 mm. The 2,4-tolylene diisocyanate was obtained from the Canadian Armaments Research and Development Establishment at Valcartier, Que. It was treated as were the other isocyanates; the boiling point was 165° C at approximately 50 mm.

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Urethanes were prepared by causing isocyanate to react with a small excess of alcohol; in certain cases the reaction was catalyzed with ferric acetylacetonate. The urethanes were purified by recrystallization from petroleum ether. The urethanes of *m*-tolyl isocyanate are liquids at room temperature; they were purified by a double vacuum distillation, only the middle portion being retained in each case. In cases where the urethanes have been previously reported the melting point of the prepared material was compared with that given in the literature. In the cases of previously unreported urethanes a carbon and hydrogen analysis was carried out. For each urethane prepared, the melting or boiling point and, where appropriate, the literature melting point and the results of the elemental analysis are given in Table I.

TABLE I

Urethanes: melting points and analytical results

Urethane	M.p. (°C)	Literature m.p. (°C)	% carbon		% hydrogen	
			Exptl.	Theory	Exptl.	Theory
N-Phenyl-*n*-butyl	57.5	57 (7)				
N-Phenyl-*i*-butyl	85.5–86.0	86 (7)				
N-Phenyl-*s*-butyl	64–65	65 (7)				
N-*o*-Tolyl-*n*-butyl	45.5–46.0	45.5 (8)				
N-*o*-Tolyl-*i*-butyl	41–42		70.05	69.52	8.27	8.27
N-*o*-Tolyl-*s*-butyl	42.5–43.0		69.58	69.52	8.18	8.27
N-*m*-Tolyl-*n*-butyl	185 (b.p. at 5 mm)		69.75	69.52	8.61	8.27
N-*m*-Tolyl-*i*-butyl	183 (b.p. at 15 mm)		69.47	69.52	8.27	8.27
N-*m*-Tolyl-*s*-butyl	179 (b.p. at 20 mm)		69.53	69.52	8.67	8.27
N-*p*-Tolyl-*n*-butyl	63	63 (8)				
N-*p*-Tolyl-*i*-butyl	52.5–53.0		70.01	69.52	8.25	8.27
N-*p*-Tolyl-*s*-butyl	32–33		69.86	69.52	7.95	8.27
N,*N*′-2,4-Tolylene-di-*n*-butyl	79		63.56	63.40	7.94	8.14
N,*N*′-2,4-Tolylene-di-*i*-butyl	122–123		63.07	63.40	7.90	8.14
N,*N*′-2,4-Tolylene-di-*s*-butyl	90–91		63.57	63.40	7.95	8.14

Calorimetry

The heats of reaction were measured using a differential microcalorimeter of the Tian–Calvet (9) type. The instrument was fitted with electronic amplifier and integrator circuits as described by Attree, Cushing, Ladd, and Pieroni (10). It can be shown (9) that the area under the curve of amplified thermopile voltage vs. time is directly proportional to the amount of heat which produces the thermopile voltage. It was found experimentally that equal amounts of heat, liberated simultaneously in each cell of the calorimeter, gave rise to a net area of zero, indicating that the two opposing thermopiles are properly balanced.

The calorimeter was calibrated electrically; a curve of total area against heat was constructed by liberating various amounts of heat in the reaction cell of the calorimeter, and recording the resulting area. Because of a tendency for the electronic components of the system to drift, the calibration was checked after every measurement. This was done by duplicating, by electrical heating, the area due to the chemical reaction. The electrical calibration procedure was checked by measuring the heat of solution of anhydrous lithium sulphate crystals in water. The heat of solution for the process

$$\mathrm{Li_2SO_4\,(c.) + 220H_2O\,(l.) = Li_2SO_4.220\,(aq.)}$$

was found to be -6.54 ± 0.10 kcal mole^{-1}. This is in good agreement with the value of -6.61 kcal mole^{-1} obtained from the N.B.S. tables (11).

In order to compensate for the heat evolved on mixing the alcohol and isocyanate reactants, an amount of urethane equivalent to the amount of isocyanate was dissolved in one cell of the calorimeter, while the reaction took place in the other cell. Since the calorimeter is a differential one, the net heat measured was that due to the heat of reaction.

The reaction cell assembly consists of a stainless steel capsule, with ends of aluminum foil, containing either the isocyanate or the urethane. It is suspended in a glass cylindrical cell which contains the alcohol. The reaction is initiated by piercing the ends of the cylinder with a length of wire held in place directly above the capsule. There is a calibrating resistor in the cell containing the isocyanate. The cells are stirred gently during the initial period of the reaction by a mechanical suction device; stirring was necessary to obtain reproducible results.

There is a tendency towards the formation of disubstituted ureas instead of urethanes during alcohol–isocyanate reactions. The tendency increases on going from normal to secondary to tertiary alcohols, and also as the temperature increases (5). Dyer *et al.* (5) report urea formation during the reaction between phenyl isocyanate and secondary-butyl alcohol at 25° C. None was observed under our reaction conditions. Because of the possibility of side reactions, however, the product of each reaction was examined in the following way. The solution of the product in alcohol (the final state after reaction) was examined for the presence of crystals of the disubstituted urea (these ureas are insoluble in the butyl alcohols). The excess alcohol was removed under vacuum and an infrared spectrum of the solid product was taken. This was compared with the spectrum of the expected urethane, obtained from the previously prepared material. Only in the case of the reaction between *p*-tolyl isocyanate and secondary-butyl alcohol was there evidence of appreciable side reaction. Since only a few insoluble crystals were seen in the reaction vessel, the side reaction was estimated to involve less than 5% of the isocyanate. No correction to the observed heat was made; such a correction will be small since the reaction involving tertiary-butyl alcohol, which yields considerable urea, gives approximately the same heat of reaction as do the reactions which yield only urethane as product.

The calories used in this paper are defined calories, equal to 4.1840 joules.

EXPERIMENTAL RESULTS

The heats evolved per mole when normal-, iso-, and secondary-butyl alcohols react with phenyl isocyanates, the three tolyl isocyanates, and 2,4-tolylene diisocyanate, are given in Table II. In the table the weight of isocyanate used is given, as well as the heat measured experimentally. The measured heat is the heat evolved when the given weight of isocyanate is introduced into 10 ml of the given alcohol, less the heat evolved when a weight of urethane equivalent to the isocyanate is dissolved in 10 ml of the alcohol. The heat of reaction in kcal mole^{-1} calculated from the measured heat is also given in the table. The molecular weights of the isocyanates were taken to be for phenyl, 119.12; for tolyl, 133.14; and for 2,4-tolylene diisocyanate, 174.06.

In the case of certain reactions, a catalyst was used to shorten the reaction time and decrease the experimental error due to drift in the electronic components of the calorimeter over long periods of time. The heats of reaction measured in the presence of a catalyst are clearly marked in the table. In order to be certain that the added catalyst did not affect the heat of reaction, certain reactions were measured with and without a catalyst. As expected, the presence of catalyst does not affect the heat of reaction. The catalysts used were either ferric acetylacetonate or dimethylcetylamine.

Although the experimental deviation is usually less than $\frac{1}{2}$% for each reaction, we have attached a somewhat larger experimental error to our work because of our inability to detect side reactions, unless they are appreciable. The estimated error for each reaction is given in the table.

DISCUSSION

The heats of alcohol–isocyanate reactions do not appear to have been previously measured, and there are insufficient heat of formation data to permit their calculation. Consequently no comparison with previous measurements is possible. The heats of formation of the isocyanates can, however, be estimated using an empirical bond energy scheme. The scheme used is that devised by Laidler (12) together with certain modifications to it which are applicable to aromatic ring compounds.

Lemoult's value for the heat of combustion of ethyl isocyanate (424.4 kcal mole^{-1}) has been used without correction to calculate the heat of atomization of ethyl isocyanate as 976.3 kcal mole^{-1}. The bonds contributing to this value are

$$c_1+3p+2s+n = 976.3,$$

where, following Laidler, the carbon–carbon bond energy is c_1, primary carbon – hydrogen bonds are represented by p, and secondary carbon – hydrogen bonds by s. The contribution to the heat of atomization by the isocyanate group is denoted by n. Laidler gives values of 85.40, 98.96, and 98.23 kcal for the contributions to the heat of atomization of a compound in the liquid state for c_1, p, and s respectively. From these values

TABLE II

The heats of isocyanate reactions at 25° C

n-Butyl alcohol			*i*-Butyl alcohol			*s*-Butyl alcohol		
Weight of isocyanate (g)	Observed heat of reaction (cal)	Heat of reaction (kcal mole^{-1})	Weight of isocyanate (g)	Observed heat of reaction (cal)	Heat of reaction (kcal mole^{-1})	Weight of isocyanate (g)	Observed heat of reaction (cal)	Heat of reaction (kcal mole^{-1})
Phenyl isocyanate								
0.1305	27.36	24.97*	0.1292	26.17	24.13	0.1204	23.72	23.47
0.1259	26.50	25.07*	0.1264	25.52	24.05	0.1174	23.02	23.36
0.1449	30.45	25.03*	0.1282	26.00	24.16	0.1166	22.92	23.42
0.1474	31.10	25.12						
0.1155	24.32	25.08						
		Mean 25.1±0.3			Mean 24.1±0.3			Mean 23.4±0.3
o-Tolyl isocyanate†								
0.1257	22.10	23.41	0.1199	19.90	22.10	0.1267	20.65	21.70
0.1198	21.04	23.38	0.1280	21.15	22.00	0.1263	20.53	21.64
0.1168	20.60	23.48	0.1281	21.25	22.09	0.1257	20.55	21.76
0.01605	2.840	23.55	0.1168	19.84	22.16			
		Mean 23.5±0.3			Mean 22.1±0.3			Mean 21.7±0.3
m-Tolyl isocyanate‡								
0.1784	26.11	19.49	0.1750	25.10	19.10	0.1918	26.65	18.50
0.1692	24.84	19.55	0.1779	25.52	19.10	0.1848	26.05	18.55
0.1710	25.00	19.46	0.1809	25.89	19.05	0.1811	25.21	18.53
		Mean 19.5±0.3			Mean 19.1±0.3			Mean 18.5±0.3
p-Tolyl isocyanate§								
0.1370	25.44	24.74	0.1405	25.35	24.02	0.1534	27.12	23.54
0.1236	22.98	24.75	0.1291	23.23	23.96	0.1537	27.10	23.47
0.1222	22.65	24.68	0.1315	23.60	23.90‖	0.1482	26.45	23.76
0.1198	22.30	24.78	0.1311	23.50	23.86‖	0.1548	27.50	23.65
0.1191	22.10	24.71				0.1485	26.35	23.62
		Mean 24.7±0.3			Mean 23.9±0.3			Mean 23.6±0.6
2,4-Tolylene diisocyanate¶ **								
0.1114	28.18	44.03	0.0944	23.11	42.61	0.0879	20.86	41.31
0.1008	25.46	43.96	0.1005	24.67	42.73	0.943	22.40	41.35
0.1012	25.58	44.00	0.0939	22.90	42.45	0.1077	25.60	41.37
0.0951	24.04	44.00	0.1011	24.85	42.78	0.1034	24.58	41.38
		Mean 44.0±0.6			Mean 42.6±0.8			Mean 41.3±0.6

*Reaction catalyzed by dimethylcetylamine (0.05 g/100 ml alcohol).

†Reaction with *i*-butyl alcohol catalyzed with ferric acetylacetonate (0.15 g/100 ml alcohol).

‡The urethanes of *m*-tolyl isocyanate are in the liquid state at 25° C.

§A small amount of *N*,*N*′-di-*p*-tolyl urea was formed in reactions with *s*-butyl alcohol. The amount is estimated to be less than 5%.

‖Reaction catalyzed with ferric acetylacetonate (0.15 g/100 ml alcohol).

¶*N*,*N*′-2,4-tolylene di-*i*-butyl urethane is slow to dissolve in *i*-butyl alcohol. It was necessary to stir the second cell violently to achieve solution, with a considerable decrease in experimental reproducibility.

**Reactions with *i*- and *s*-butyl alcohol catalyzed by ferric acetylacetonate (0.15 g/100 ml alcohol).

and the heat of atomization of ethyl isocyanate, the value of n, the bond energy of the isocyanate group, is calculated to be 397.6 kcal. Preliminary work on a bond energy scheme for aromatic compounds indicates that carbon–carbon bonds in an aromatic ring should have a special value, denoted by c_b, as should carbon–hydrogen bonds, denoted by t_b, when the carbon atom is part of the ring. Values of 124.29 and 97.55 kcal for c_b and t_b respectively have been used. The heat of atomization of phenyl isocyanate is given by $6c_b+5t_b+n$, yielding a value of 1631.01 kcal mole^{-1} for the heat of atomization of liquid phenyl isocyanate; from this, $\Delta H_f{}^0$ (l., 25° C) = 3.5 kcal mole^{-1} is obtained. Similarly, for the tolyl isocyanates, $\Delta H_f{}^0$ (l., 25°) is found to be -5.3 kcal mole^{-1}. There are insufficient data available to attempt to make allowance in $\Delta H_f{}^0$ for the ring positions of the three tolyl isocyanate isomers. It is expected that two isocyanate groups on an aromatic ring would lead to considerable interaction; this would affect the heat of formation which, therefore, has not been calculated for 2,4-tolylene diisocyanate.

The heats of formation of the urethanes are readily approximated using the heats of formation of the alcohols, the estimated heats of formation of the isocyanates, and the appropriate heat of reaction.

The results of the heat of reaction measurements can be interpreted in terms of substituent effects. As far as the effect of changing the alcohol from normal- to iso- to secondary-butyl is concerned, a decrease in stability of the resulting urethane (the heat of reaction being a measure of the stability of the resulting urethane) would be expected on the grounds of steric hindrance. The inductive effect will act in the same direction, tending to put a partial negative charge on to the urethane group. This will decrease the resonance stabilization of the urethane group with the aromatic ring to which it is attached. It is observed in the case of every isocyanate that the heat of reaction decreases in the order normal > iso > secondary. Turning to the effects of a methyl group substituted into the aromatic ring of the urethane, it is expected that partial negative charges would appear ortho and para to the methyl group, due to the resonance effect. There will be, in addition, a small charge on the ring due to the inductive effect, which decreases in the order ortho > meta > para. Steric effects will also be of importance in cases of ortho substitution. From these considerations phenyl isocyanate should show the largest heat of reaction, *m*-tolyl isocyanate would be expected to yield a smaller value, followed by *p*-tolyl isocyanate. Because of the steric effect, the heat of formation of ortho urethanes should be considerably less than for the others. These predictions are substantiated by the experimental results; because of the difference in state the predicted behavior of *m*-tolyl isocyanate reactions cannot be verified.

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