centers is 2.4–2.5 Å.[14] It is our contention that, considering the space occupied by the extended oxygen π orbitals possessing the bulk of the electron density, this is not a sufficient separation[15] to accommodate a sodium ion (diameter 1.90 Å). A similar model for adipamide (Figure 3b) gives a maximum distance between oxygens of 3.8–4.0 Å with enough flexibility in the carbon chain to adjust downward to whatever minimum-energy dimension is required by the cation. The even greater distance afforded by the pimelamide provides no further advantage, since the optimum has been reached in the adipamide. Indeed, the larger number of conformational degrees of freedom in the pimelamide results in a less favorable entropy for disolvation so that its activity decreases with respect to the adipamide. Presumably, further chain extension would provide even less intramolecular synergism, and catalytic activity would approach that of *N,N*-dimethylacetamide.

An alternate mechanism involving intramolecular π-donor–π-acceptor solvation of both ions of the ion pair (Figure 3c) is not considered to be important for three reasons: (1) it is not likely that the steric demands for simultaneous and optimal solvation of both a small cation and a large anion could be met by any such scheme; (2) in fact, it is known[17] that dipolar aprotic compounds usually coordinate with small cations more readily than with anions; and (3) the anion in such a solvated ion pair would not possess greatly increased nucleophilic reactivity, because any decrease in sodium-ion influence would be offset by the proximity of the two positively charged nitrogen atoms.

The low activity of the other diamides compared to the standard monoamide shows that the second amide group is actually counterproductive with respect to cation solvation. Part of this effect, especially for the lower homologs, may be steric.[12] However, the abnormally low dielectric constant for the succinamide (Figure 2) suggests the occurrence of considerable intramolecular neutralization of the amide dipoles. This would tend to reduce the π-donor capacity of either amide function below that of the monoamides in which such interaction occurs only through intermolecular association. The highly active adipamide also shows some evidence of such intramolecular amide interaction. In the presence of sodium ion, however, the capacity of the two functions to act synergistically (*cf.* Figure 3b) clearly supplants the deactivating effect of the dipole neutralization.

Registry No.—$HCON(CH_3)_2$, 68-12-3; $[CON(CH_3)_2]_2$, 1608-14-6; $(CH_2)_2[CON(CH_3)_2]_2$, 7334-51-2; $(CH_2)_4[CON(CH_3)_2]_2$, 3644-93-7; $(CH_2)_5[CON(CH_3)_2]_2$, 34712-64-6; diethyl *n*-butylsodiomalonate, 22600-93-7; *n*-butyl bromide, 109-65-9.

[14] A similar model of succinamide shows that the collinear requirement cannot be met.

[15] Although the "hole" in dicyclohexyl-18-crown-6 polyether is not much larger than this (2.6–3.2 Å),[16] the space occupied by the oxygen n orbitals in ethers is considerably less than that required by the π orbitals in amides.

[16] C. J. Pedersen, *J. Amer. Chem. Soc.*, **92**, 386 (1970).

[17] A. J. Parker, *Quart. Rev., Chem. Soc.*, **16**, 163 (1962).

Thermal Reactions of Alkyl Isocyanates. I

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The gas-phase thermal reactions of alkyl isocyanates have been investigated using a static manometric technique. While the ethyl compound decomposes through a complex and partly heterogeneous series of reactions, isopropyl and *tert*-butyl isocyanates yield isocyanic acid and olefins by a well-defined, homogeneous, first-order process. The effect of temperature on the rate constants is given by the following equations: isopropyl isocyanate, $\log k_1 \, (\mathrm{sec}^{-1}) = 12.71 - (53{,}300/2.30RT)$; *tert*-butyl isocyanate, $\log k_1 \, (\mathrm{sec}^{-1}) = 13.59 - (52{,}400/2.30RT)$. The results are discussed with special reference to those for alkyl isothiocyanates. It is found that substitution of sulfur by oxygen in these species results in a decrease in reactivity of three orders of magnitude. The transition state for these reactions is regarded as a six-centered structure of moderate polarity.

The results previously obtained with isothiocyanates[1] have prompted us to investigate the thermal reactions of organic isocyanates in the gas phase. The most relevant work in this field has been that of Back, *et al.*, on the photolysis[2] and the pyrolysis[3] of isocyanic acid itself at temperatures above 550°. These authors conclude that the thermal decomposition of isocyanic acid occurs through a complex mechanism of appreciable heterogeneous character. Preliminary experiments carried out in these laboratories on ethyl isocyanate between 440 and 500° showed that this, too, is a complex reaction of no well-defined stoichiometry and which is presumably heterogeneous to a large extent. The situation is complicated by the tendency of this compound to polymerize in the liquid state through a reaction which appears to be catalyzed by traces of a variety of substances, among which are the products of the pyrolysis. On the other hand, isopropyl and *tert*-butyl isocyanates decompose in carbon-coated vessels in a much simpler manner. The purpose of this work is to investigate this last reaction and to compare the results with those from the sulfur analogs, namely, alkyl isothiocyanates, in an attempt to draw general conclusions about the mechanism of elimination of pseudohalides of type RXCY (X,Y = O,S,N).

Results

Isopropyl Isocyanate.—When the pyrolysis occurs in a clean Pyrex reaction vessel, the initial rate of pressure increase was erratic, and CH_4, CO, and CO_2

[1] (a) N. Barroeta, Ph.D. Thesis, University of London, 1968; (b) N. Barroeta, A. Maccoll, and A. Fava, *J. Chem. Soc.*, 347 (1969).

[2] R. Back and R. Ketcheson, *Can. J. Chem.*, **46**, 531 (1968), and references therein.

were detected in the products. If the reaction vessel was "seasoned" by the allyl bromide technique, followed by repeated pyrolysis of isopropyl isocyanate, a gradual suppression of these gases was achieved and the initial rate attained a reproducible value. The initial behavior could, however, be restored by admission of air into the vessel, although this "memory effect" was lost after four or five runs.

In a well-coated vessel the stoichiometry reduces to the simple form shown in eq 1. Confirmation for

$$(CH_3)_2CHNCO \xrightarrow{k_1} HNCO + CH_3CH{=}CH_2 \qquad (1)$$

this was achieved in three ways. (a) An increase in the total pressure to a maximum value of twice the initial pressure was observed. (b) Careful analysis of the reaction mixture showed that isocyanic acid and propylene were the only products present in detectable quantities. The ir spectrum of the acid produced corresponds completely to that of isocyanic acid as reported by Herzberg and Reid.[4,5] (c) The proposed stoichiometry corresponds to the experimentally determined amounts of reaction products (Table I).

Table I

Product Analysis in the Pyrolysis of Isopropyl Isocyanate

Compound analyzed	Temp, °C	% reaction from pressure	% reaction from direct analysis
$i\text{-}C_3H_7NCO$	413.0	8.7	11.1[a]
	413.0	20.7	23.1[a]
	413.0	26.9	26.3[a]
Propylene	413.0	10.4	8.9[b]
	413.0	18.9	19.0[b]
	413.0	24.7	22.8[b]
	413.0	33.3	32.0[b]
	440.8	14.8	14.5[c]
	440.8	25.6	25.4[c]
	440.8	39.5	37.4[c]
	440.8	42.2	49.0[c]
	440.8	57.7	56.5[c]
	440.8	70.1	69.3[c]
	440.8	86.1	85.1[c]
	480.4	50.8	50.5[c]
	480.4	58.8	57.4[c]
	480.4	64.2	65.4[c]

[a] By method A. [b] By method B. [c] By method C.

Kinetics.—For runs made in nonseasoned vessels, the initial rate is large (Table II), relative to those runs made in perfectly coated ones, and the first-order rate constant falls steadily with time. This behavior is related to the fact that values of $\Delta P_{\text{total}}/P_{\text{propylene}}$ of the order of 1.30 were observed and, on the whole, indicates that a complex heterogeneous reaction, probably involving both isocyanic acid and isopropyl isocyanate, is set up. To overcome these difficulties the kinetic study was carried out in a reactor having a surface to volume ratio of 0.8 cm^{-1} and which had been seasoned previously by repeated pyrolysis of isopropyl isocyanate. Under these conditions the production of permanent gases was suppressed and all heterogeneous processes were reduced to a negligible extent as can be ascertained from Table II. The first-order nature of the reaction follows from the observed proportionality between initial velocity (V_0) and initial pressure of reactant (P_0). According to this relationship the first-order-rate constants (Table III) were calculated as

$$-k_1 = t^{-1} \ln|(2P_0 - P)/P_0|$$

Table II

Effect of Surface on Reaction Velocity for C_3H_7NCO

Temp, °C	A/V, cm^{-1}	Reactor's surface	$k_1^{\text{exp}} \times 10^4$ sec^{-1}	$k_1^{\text{calcd}} \times 10^4$ sec^{-1} [a]
413.5	4.0	Clean	4.07	0.538
413.5	4.0	Coated	1.78	0.538
426.5	4.0	Coated	1.37	1.16
447.1	4.0	Coated	4.41	3.46
459.0	4.0	Coated	7.50	6.52
471.0	4.0	Coated	13.00	11.4
484.0	4.0	Coated	19.6	21.1

[a] By calculated rate constant (k_1^{calcd}) is meant the value computed from the Arrhenius equation obtained when the reaction is studied in a "coated vessel" with a surface to volume ratio of 0.80 cm^{-1}.

Table III

First-Order Rate Constants at Varying Initial Pressures

Temp, °C	P_0 of C_3H_7NCO, mm	$k_1 \times 10^4$ sec^{-1}
440.8	132	2.66
440.8	166	2.62
440.8	180	2.40
440.8	239	2.43
440.8	434	2.73
498.1	70	39.3
498.1	145	40.2
498.1	190	38.8
498.1	240	37.2

To check on the possibility of chain mechanisms, rate constants were determined from runs to which a variety of radical chain inhibitors were added, but only a very small decrease in rate was observed and this was apparently not connected with the relative amount of inhibitor used (Table IV).

Table IV

Effect of Inhibitors on Reaction Velocity in the Pyrolysis of Isopropyl Isocyanate

Inhibitor	% inhibitor	Temp, °C	$k_1^{\text{found}}/k_1^{\text{calcd}}$	$k_1^{\text{found}}/k_1^{\text{none}}$ [a]
Nitric oxide	22.2	425.8	0.937	0.981
	21.3	467.0	0.922	0.873
	24.6	467.0	1.06	1.01
Propylene	68.6	440.8	0.936	0.915
	113.4	440.8	0.930	0.909
	42.8	467.0	0.902	0.855
	58.2	467.0	0.996	0.944
	94.6	467.0	0.932	0.883
	39.4	480.4	0.897	1.05
	85.5	480.4	0.855	1.00
Cyclohexene	72.2	464.0	0.936	
trans-Butene-2	75.0	464.0	0.881	

[a] Experimental value of k_1 for the unperturbed reaction: none = no additive. These runs were made from the same sample of isocyanate and immediately before the inhibition experiments and thus give an idea of the reproducibility of the rate constants through a comparison between k_1^{calcd} and k_1^{none}.

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(4) C. Reid, *J. Chem. Phys.*, **18**, 1544 (1950).

(5) G. Herzberg and C. Reid, *Trans. Faraday Soc.*, **46**, 92 (1950).

The results of pyrolysis at seven temperatures within the range of 425–498° and an average of five runs at each temperature were treated by a least-squares procedure to yield the Arrhenius equation

$$\log k_1\ (\mathrm{sec}^{-1}) = 12.71 \pm 0.24 - \frac{53{,}290 \pm 800}{2.303RT}$$

***tert*-Butyl Isocyanate. Stoichiometry.**—When the thermolysis was carried out in a clean Pyrex glass reactor the occurrence of heterogeneous reactions led to irreproducibility in the rate constants, formation of permanent gases (although to a lesser extent than in the isopropyl isocyanate pyrolysis), and a marked decrease with time of the total pressure after it had attained a maximum value of $\sim 1.6P_0$. All of these complications disappeared when the reactor was conditioned by repeated pyrolysis of *tert*-butyl isocyanate itself. The remaining reaction can be presented remarkably well by eq 2 as was demonstrated by careful analysis of the reaction mixture. In Table V the extent of the reaction as given by pressure measurements is compared with the same quantity calculated from direct determination of the reaction products.

$$(CH_3)_3CNCO \xrightarrow{k_1} (CH_3)_2C{=}CH_2 + HNCO \qquad (2)$$

TABLE V

VALIDITY OF PRESSURE READINGS AS A MEASURE OF THE EXTENT OF REACTION IN THE PYROLYSIS OF *tert*-BUTYL ISOCYANATE

Compound analyzed	Temp, °C	% reaction from pressure	% reaction from direct analysis	
			Method A	Method B
2-Methylpropene	410.0	23.0		23.2
	410.0	35.6		34.3
	410.0	55.3		54.7
	410.0	72.2		70.1
	410.0	86.0		86.5
	410.0	96.0		94.2
tert-Butyl isocyanate	400.0	22.9	24.4	
	410.0	9.0	9.1	
	410.0	19.6	19.9	
	410.0	31.3	31.9	
	410.0	45.4	48.0	
	420.0	28.9	27.5	
	420.0	43.9	46.0	
	420.0	50.7	50.6	

A further test on the stoichiometry was performed by titration of the total isocyanate (*tert*-butyl isocyanate plus isocyanic acid) present in the reaction mixture with *tert*-butylamine according to Wild's method.[6] This should give 100% relative to the initial pressure. The mean value of 14 determinations distributed within the first half-life of the reaction was 100.0 ± 1.6, thus confirming reaction 2.

Kinetics.—The total pressure increase followed the first-order rate law until the reaction was at least 50% complete and this equation was used to calculate first-order rate constants. No trend was observed when the initial concentration was varied by a factor of 13.

Attempts to modify the value of the rate constant by increasing the surface to volume ratio of the reactor by a factor of 4 were unsuccessful as was the addition of propene and cyclohexene in amounts as high as 120%.

The temperature dependence of the rate constant was found to obey the Arrhenius equation

$$\log k_1\ (\mathrm{sec}^{-1}) = 13.59 \pm 0.29 - \frac{52{,}380 \pm 540}{2.303\ RT}$$

This equation was obtained by the least-squares method from experiments made at nine temperatures within the interval of 380–440°.

Discussion

In agreement with the pattern shown in the pyrolysis of other substances such as alkyl halides and esters, the complexity of these reactions greatly decreases when going from ethyl to *tert*-butyl derivatives. As explained above, heterogeneous reactions, although present when all the isocyanates were studied in clean Pyrex glass reactors, can be eliminated by properly covering the walls of the reactor with carbonaceous films arising from the pyrolysis of isocyanates themselves. An exception to this was the pyrolysis of ethyl isocyanate which is complex under any condition. On the other hand, we believe that the results of the experiments in which the nature and extent of reactor's surface was varied are sufficient evidence of homogeneous mechanism in the cases of isopropyl and *tert*-butyl isocyanates. We further propose that these latter reactions are unimolecular eliminations. The evidence for this comes from a consideration of several facts which can be summarized as follows. In the first place, the reactions obey a first-order kinetic law. Secondly, the increase in total pressure follows a well-defined, exponential form with no observable induction periods. Thirdly, a careful analysis of the products reveals an uncomplicated stoichiometry. A radical chain reaction would yield detectable amounts of by-products unless the chain length is very large, and the isocyanate radical is not expected to propagate such chains. Fourthly, the reactions are not significantly affected, either in the rate or in the distribution of products by the addition of well-known inhibiting substances like propene, cyclohexene, and nitric oxide. Finally, the experimental Arrhenius parameters are better understood in terms of a molecular split into isocyanic acid and olefin. If a radical nonchain mechanism with the homolytic breakage of the C–N bond as the rate-controlling step were operating, one would expect a larger *A* factor and an activation energy equal or higher than the dissociation energy of that bond. Although no direct measure of this quantity has been published one can make a reasonable estimate on two different grounds. Firstly, if one accept 100 kcal/mol as the lower limit for the H–NCO bond[7] one can easily work out a lower limit of 73 ± 3 kcal/mol for the C–N bond in methyl and ethyl isocyanates through enthalpies of formation of molecules[8] and radicals.[9] Secondly, preliminary work on electron-impact phenomena on *tert*-butyl isocyanate yields a lower limit for the dissociation energy of the C–NCO bond of 74 kcal/mol *via* the appear-

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[6] F. Wild, "Estimation of Organic Compounds," Cambridge University Press, Cambridge, p 201, 1953.

[7] W. D. Wooley and R. A. Back, *Can. J. Chem.*, **46**, 295 (1968).

[8] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., p 631, 1969.

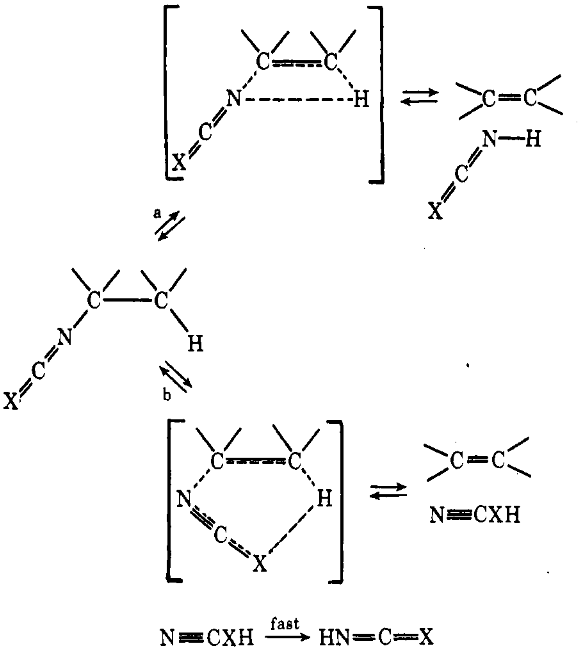
[9] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

ance potential[10] of $C_4H_9^+$ and the ionization potential of the *tert*-butyl radical.[11] The difference between this values and the observed activation energies is far too great to be explained by the inaccuracies in the estimates so that this mechanism can be safely dismissed.

One of the reasons for studying the thermolysis of isocyanates was to investigate the effect of atomic substitution within the pseudohalogen moiety in the hope that the results could be useful when discussing the nature of the transition state of the isothiocyanate elimination reaction. We have pointed out[1] that for this reaction there exists an ambiguity about the structure of the transition state, namely, that a four-center reaction yields isothiocyanic acid directly (Scheme I, path a) or a six-center reaction initially forms thiocyanic acid which then isomerizes very rapidly to isothiocyanic acid (Scheme I, path b). We have been inclined to favor the former structure on steric and electronic grounds,[1,12] the problem at hand being related to that of the actual existence of species H–OCN and H–SCN in the gas phase which has been discussed by several authors.[4,5,13,14]

SCHEME I

THE TWO POSSIBLE TRANSITION STATES FOR PSEUDOHALIDES OF ALLENIC STRUCTURE (X = S, O)



As pointed out above, the acid produced in the pyrolysis of isopropyl and *tert*-butyl isocyanates, as well as for thio- and isothiocyanates, was that tautomer with the hydrogen attached to nitrogen. This fact, together with the alleged[1,12] structural difficulty to "close" a six-membered ring and the availability of sp^2 unpaired electrons on nitrogen, suggest a four-center transition state, although it is now realized that a reaction which could presumably be correlated to this structure, namely, the unimolecular split of *tert*-butylamine,[15] has a much higher activation energy and this could be taken as evidence against it.

The sulfur-for-oxygen substitution is accompanied by changes in the electronic distribution with profound bearings on the reaction. One may take the atomic charges calculated by Wagner[16] for HNCS and HNCO as a first approximation to the problem. According to this charge distribution, the negative atomic charge is diminished at both ends of the isocyanate group in relation to the sulfur analogs. This could explain, at least in part, why the activation energies for the isocyanates are ~13 kcal/mol higher than for the corresponding isothiocyanates which means a factor of three orders of magnitude in the relative rates (Table VI). Because of this large difference in reactivity, one is inclined to conclude that the oxygen and sulfur atoms must be directly involved in the reaction center rather than acting indirectly on the nitrogen atom. This being more so when one considers that, because of the particular geometry of the π orbitals within the NCO group, the β hydrogen "does not see" the electronic changes in the orbital associated with nitrogen whereas the C–N π orbital, being at right angles to the former, is particularly suited for an initial attack on the β hydrogen and changes on this orbital should be reflected more effectively in the reactivity. This view is reinforced by the fact that a similarly large difference in reactivity exists between xanthates and carboxylic and carbonate esters where doubly bonded oxygen and sulfur abstract a β hydrogen in a six-center transition state.[17] Furthermore, in spite of the above-mentioned steric restriction, this structure is not unattainable for isothiocyanates. On the contrary, an equivalent arrangement of atoms is generally accepted for the isomerization of allylic thiocyanates.[18]

TABLE VI

RATE CONSTANTS FOR THE REACTION $RX \longrightarrow HX + \text{OLEFIN AT } 440.8°$

Reactant	$k_1 \times 10^4$, sec^{-1}	k_1 (t-C_4H_9X)/ k_1 (i-C_3H_7X)	Reference
C_3H_7NCS	7346.0		16
t-C_4H_9NCS	84240.0	11.5	16
i-C_3H_7NCO	2.49		This work
t-C_4H_9NCO	36.6	14.5	This work
i-$C_3H_7OCOCH_3$	1690.0		*a*
t-$C_4H_9OCOCH_3$	81000.0	47.9	*a*
tert-Butyl-NH_2	0.0053		15

[a] Preferred value: S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," U. S. Department of Commerce, Washington, D. C., Publication NSRDS-NBS-21, pp 169, 189, 1970.

As is apparent from the discussion above, the transition state for elimination in molecules of type RNCX (X = X, O) is probably more accurately represented by a six-centered structure, contrary to our previous views,[12] although the initial interaction between the

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(10) A. Maccoll, private communication.

(11) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, U. S. Department of Commerce, Washington, D. C., Publication NSRDS-NBS 26, p 14, 1969.

(12) N. Barroeta, A. Maccoll, M. Cavazza, L. Congiu, and A. Fava, *J. Chem. Soc.*, 1267 (1971).

(13) N. Groving and A. Holm, *Acta Chem. Scand.*, **19**, 1768 (1965).

(14) C. I. Beard and B. P. Dailey, *J. Chem. Phys.*, **15**,762 (1947).

(15) H. O. Pritchard, R. G. Sowden, and A. I. Trotman-Dickenson, *J. Chem. Soc.*, 546 (1954).

(16) E. L. Wagner, *J. Chem. Phys.*, **43**, 2728 (1965).

(17) C. H. De Puy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

(18) A. Fava in "The Chemistry of Sulfur Compounds," N. Kharash and C. Meyers, Ed., Pergamon Press, Oxford, p 73, 1966.

hydrogen and the -NCX group could be through the π orbitals of the C=X bond. However, this formulation leaves unanswered the fact that only HNCO and HNCS are detected in the products, although under the conditions of our analysis, namely, at least 25% decomposition and in a 10-cm ir gas cell, this could be accounted for if the rate constant of isomerization of these species is at least twenty times larger as that for elimination. We plan to do more work along these lines and to extend the investigation to the isoselenocyanates.

An indication of the degree of polarity of the reaction is obtained from Table VI where a similar effect of α-methylation on rate is observed for isocyanates and isothiocyanates suggesting identity of mechanism. The absolute magnitude of this effect, although comparable with that found in the acetates, is much less than in the case of alkyl halides, a reaction regarded as quasiheterolytic.[19]

Experimental Section

An all-glass apparatus of conventional design was used. The reaction vessel was a cylinder of about 380-ml capacity and fitted with a glass-diaphragm gauge which allowed the kinetics to be followed manometrically. The temperature of the furnance was kept constant within 0.2° by means of an RT5 Mk.2 temperature controller from Associated Electrical Industries, England.

Reagents.—Isopropyl and *tert*-butyl isocyanates were laboratory reagents from K & K Laboratories, Inc., that had been fractionated to give a purity better than 99.9% as established by gas chromatography using a flame ionisation detector.

Quantitative Analysis.—Method A was used for determination of the starting material by the internal standard technique. The reaction mixture was condensed, at liquid nitrogen temperature, directly in a trap containing a known amount of the standard. For this purpose, *n*-heptane and toluene were used for the determination of isopropyl and *tert*-butyl isocyanates, respectively. The factors used to convert chromatographic area ratios into pressure ratios were found to be 3.17 ± 0.15 and 1.92 ± 0.09 for the flame ionisation detector.

Method B was used for the analysis of olefins. The reaction mixture was removed from the reactor and passed through a column filled with soda-lime followed by a trap at −80°. The olefin was finally condensed at liquid nitrogen temperature in a bulb containing the standard. Isobutylene and propylene were determined in this manner with *n*-butane as a standard. The calibration factors were 0.934 ± 0.042 and 1.26 ± 0.07, respectively.

Method C was employed for the determination of propylene and was similar to method B except that the final bulb was calibrated and the amount of gas computed from P, V, and T measurements.

Instrumental Analysis.—The reaction products were identified by a combination of several physical methods of analysis which included gas chromatography with Perkin-Elmer F11 apparatus fitted with both thermal conductivity and flame ionisation detectors. For the gas chromatography–mass spectrometry technique a Perkin-Elmer 990 chromatograph coupled to a Hitachi Perkin-Elmer RMU-6H mass spectrometer was used. Ir analysis of gases were carried out in a Perkin-Elmer 337 grating spectrophotometer fitted with a 10-cm gas cell. Nmr analysis of the hydrocarbon fraction was performed at temperatures sufficiently low to keep the sample liquid in a Varian A-60 apparatus.

Registry No.—Isopropyl isocyanate, 1795-48-8; *tert*-butyl isocyanate, 1609-86-5.

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(19) A. Maccoll, *Chem. Rev.*, **69**, 32 (1969).

Diquaternary Salts. I. Preparation and Characterization of the Diquaternary Salts of Some Diazines and Diazoles[1]

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By using oxonium salts as alkylating agents, diquaternary salts of pyrazines, pyrimidines, pyridazines, triazoles, and thiadiazoles have been prepared for the first time. Structures were established by a combination of spectroscopic and chemical techniques. Pyrazinium diquats were found to undergo spontaneous radical cation formation upon solution in alcohols, whereas pyrimidinium salts did not. A rationale for this in terms of HMO theory is presented.

Many monocyclic diaza aromatics, including pyrazines, pyrimidines, pyridazines, and various diazoles, possess two nitrogen atoms whose unshared electron pairs are not part of a π-electron system. While in principle, such molecules could form diquaternary salts without loss of aromaticity, in practice diquaternization has apparently never been observed.[2] Thus Bahner and Norton obtained only monoquaternary salts from the reaction of pyrazine with excess phenacyl bromide,[3] and Blood and Noller were unable to diquaternize pyridazine with *cis*-1,4-dibromo-2-butene, even though intramolecularity favored the second alkylation step.[4] Undoubtedly, these failures arise from the expected reduction in nucleophilicity of the second nitrogen attendant upon quaternization of the first. An estimate of the magnitude of this effect can be made by assuming that nucleophilicity and basicity are roughly parallel. The two K_a's of pyrazine, for example, differ by over six powers of ten.[5] A similar difference in the nucleophilicities of the dibase and of its monoquaternary salt might be expected, and therefore failure to observe diquaternization is not surprising. It seemed to us that the presence of two positive charges in a conjugated ring might be expected to lead to enhanced reactivity, and we have therefore undertaken an investigation of the preparation and properties of diquaternary salts. An additional stimulus for this work

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[1] Taken in part from the Ph.D. thesis of K. S. Prasad, St. Louis University, 1970. For a preliminary communication see T. J. Curphey, *J. Amer. Chem. Soc.*, **87**, 2063 (1965).

[2] For a review on quaternization of heterocycles see G. F. Duffin, *Advan. Heterocycl. Chem.*, **3**, 1 (1964).

[3] C. T. Bahner and L. L. Norton, *J. Amer. Chem. Soc.*, **72**, 2881 (1950). See also Y. T. Pratt in "Heterocyclic Compounds," Vol. 6, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1957, p 400.

[4] A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 844 (1957).

[5] A. S. Chia and R. F. Trimble, Jr., *J. Chem. Phys.*, **65**, 863 (1961).