

Infra-red Study of the Reactions between Ethyl Isocyanate and Silica Surfaces

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The adsorption of ethyl isocyanate from the gas phase onto silica surfaces has been investigated by infra-red spectroscopy. Products of the adsorption process include a surface urethane, 1,3-diethylurea, a biuret, dissociatively adsorbed isocyanate and ethoxy groups, and compounds formed by the polymerization of isocyanic acid and hydrogen cyanide. The relative proportions of the reaction products are sensitive to the temperature of adsorption and the temperature at which the silica surface was evacuated before exposure to the adsorbate. The formation of diethylurea only occurs when molecular water or hydrogen-bonding hydroxyl groups are present on the oxide surface. The rate of formation of diethylurea from liquid mixtures of ethyl isocyanate and water is considerably enhanced by the addition of powdered silica. The hydrolysis reaction, promoted by silica, provides a method for the rapid preparation of 1,3-diethylurea.

The formation of urethanes by the reaction of isocyanates with organic molecules containing hydroxyl-groups is well established^{1, 2}; although the possibility of interactions between isocyanates and the hydroxyl-groups on the surfaces of oxides have received little attention. There is one report that butyl isocyanate hydrogen-bonds to silica and also forms a urethane which is retained on the surface after evacuation.³ The present paper reports an infra-red study of the modifications of the surface of silica which occur following treatment with ethyl isocyanate at temperatures in the range 298-830 K.

EXPERIMENTAL

Aerosil silica (Degussa) had a surface area of *ca.* 200 m² g⁻¹. Infra-red spectra showed that the silica had adsorbed a small amount of hydrocarbon impurity which was removed by treatment in oxygen (15 kN m⁻²) at 400-500°C. Ethyl isocyanate (K and K Laboratories) was purified by cold distillation and stored over a type 4A molecular sieve. Water which had been de-ionized and distilled three times (once from alkaline potassium permanganate) all under nitrogen, and deuterium oxide (Koch-Light, purity >99.7 atom %D) were freed from permanent gases by cold pumping. B.O.C. grade X oxygen and hydrogen were used as supplied.

Infra-red spectra were measured using Perkin-Elmer 125 and 257 spectrometers which were flushed with dry nitrogen. Self supporting silica discs of 25 mm diameter and *ca.* 100 mg weight were compacted by hand pressure alone and were enclosed in infra-red cells of similar construction to those described elsewhere.⁴ The part of one cell which was enclosed by an external furnace was made of silica to allow high temperature treatment of the oxide sample. The cells were glassblown to a conventional vacuum system, fitted with greasefree taps, and capable of maintaining a dynamic vacuum of 10⁻⁴ N m⁻².

Mass spectra and n.m.r. spectra were recorded by an AEI MS 902 spectrometer and a Varian HA 100 spectrometer respectively.

RESULTS

THE ADSORPTION OF ETHYL ISOCYANATE ON SILICA AT 306 K

A silica disc was outgassed at 673 K for 9 h cooled to the ambient temperature of the spectrometer beam (*ca.* 306 K) and exposed to increasing pressures of ethyl isocyanate vapour for various times (fig. 1). The band at 3750 cm^{-1} , due to isolated hydroxyl groups on silica, and the shoulder at *ca.* 3680 cm^{-1} , which may be associated with a low residual surface concentration of adjacent hydrogen-bonded hydroxyl groups, were decreased in intensity by the adsorption of ethyl isocyanate. New bands appeared at 3670, 3440, 3330, 2985, 2943, 2889, 1697, 1635, 1555, 1525, 1479, 1455 and 1379 cm^{-1} and were stable to evacuation at 306 K.

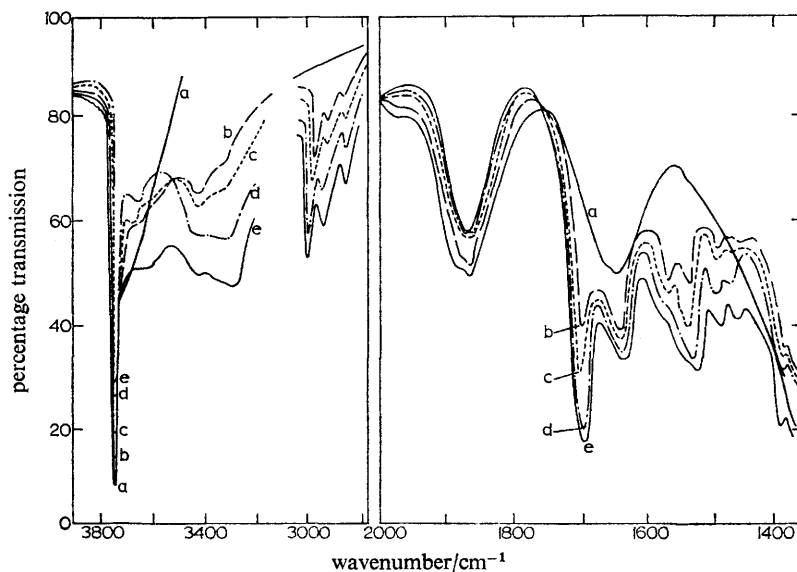


FIG. 1.—The adsorption at 306 K of ethyl isocyanate on silica which had been preheated at 673 K for 9 h. Pressures (kN m^{-2}) of adsorbate were (times of exposure in brackets): *a*, starting surface; *b*, 1.2 (2.5 h); *c*, 2.4 (2.5 h); *d*, 4.8 (16 h); *e*, 6.1 (2.5 h). All spectra were recorded after evacuation of the sample for 30 min.

The infra-red spectrum of a dilute solution of a purified sample (K and K Laboratories) of 1,3-diethylurea in carbon tetrachloride showed absorption maxima at $3350(\text{s})$, $3140(\text{vw})$, $3050(\text{vw})$, $2980(\text{w-m})$, $2938(\text{w-m})$, $2880(\text{w-m})$, $1635(\text{vs})$, $1574(\text{vs})$, $1485(\text{vw})$, $1463(\text{w})$, $1452(\text{w})$ and $1379(\text{w-m})\text{ cm}^{-1}$. The bands at 2985, 2943, 2889, 1635, 1555, 1479, 1455 and 1379 cm^{-1} for ethyl isocyanate adsorbed on silica are therefore attributed to the formation of diethyl urea as a reaction product on the surface. Adsorption on a deuterated surface caused the maximum at 1555 cm^{-1} to be shifted to lower wavenumbers and that at 1635 cm^{-1} to remain unchanged. The former band must be associated with the deformation vibration of NH groups in diethyl urea whereas the band at 1635 cm^{-1} is associated with the carbonyl stretching vibration.

The band at 1525 cm^{-1} is attributed to the formation of the surface urethane

$$\text{—Si—O—CO.NHEt}$$

when ethyl isocyanate adsorbs on silica. The band is shifted

when adsorption occurs onto a fully deuterated surface and may be assigned to the deformation vibration of NH groups. The carbonyl stretching vibration gives rise to the maximum at 1697 cm^{-1} . These assignments are consistent with published spectra of urethanes.⁵⁻⁷ The surface urethane also contributes to the bands at 2985, 2943, 2889, 1479, 1455 and 1379 cm^{-1} which are due to vibrations of CH_3 and CH_2 groups both in the urethane and in diethylurea. The bands at 3440 and 3330 cm^{-1} are assigned to the NH-stretching vibrations of unperturbed and hydrogen-bonded NHEt groups respectively in either diethylurea or the urethane.

The spectra in fig. 1 suggest that the formation of diethylurea involves hydroxyl groups which are adjacent to each other on the silica surface and does not involve isolated hydroxyl groups. Thus (fig. 1(b)) the appearance of the two strongest bands at 1635 and 1555 cm^{-1} due to diethylurea coincide with a sharp decrease in the intensity of the shoulder at *ca.* 3680 cm^{-1} (fig. 1(a)). Some urethane is also formed at the same time but results from reaction of ethyl isocyanate with isolated hydroxyl groups. Thus further reaction (fig. 1(c-e)) causes little increase in the intensities of bands (particularly that at 1635 cm^{-1}) due to diethylurea, but increases in the intensities of the urethane bands at 1697 and 1525 cm^{-1} parallel the decrease in intensity of the sharp band at 3750 cm^{-1} . The correlation is shown in fig. 2. The formation of urethane at the expense of isolated hydroxyl groups was also observed when ethyl isocyanate was adsorbed at 306 K onto silica which had previously been evacuated at 973 K. The starting surface gave a single sharp symmetrical infra-red band at 3750 cm^{-1} with no accompanying shoulder at *ca.* 3680 cm^{-1} . No diethylurea was formed during the adsorption reaction.

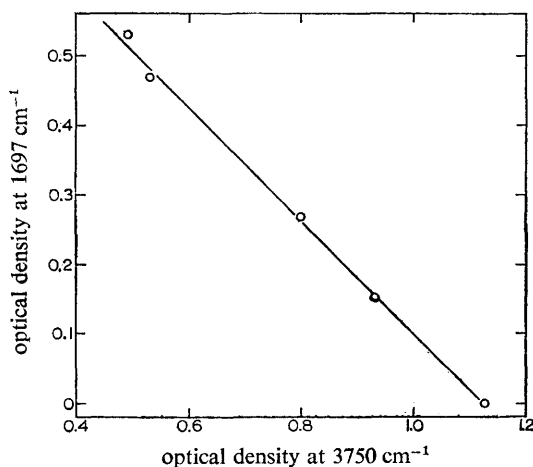


FIG. 2.—The correlation between the disappearance of isolated —SiOH groups and the appearance of a urethane when ethyl isocyanate is adsorbed on silica at 306 K. The points refer to spectra *a-e* in fig. 1.

Ethyl isocyanate was also adsorbed at 306 K onto silica samples which had been previously outgassed at 544, 439 or 406 K. A surface urethane and 1,3-diethylurea were formed in all three cases although the spectra emphasized that the formation of diethylurea rather than a urethane became more favourable the lower was the pretreatment outgassing temperature. The effect became extreme for silica which had been equilibrated with water vapour at 298 K and evacuated for only 3 min at

298 K prior to the admission of ethyl isocyanate at 306 K. The starting surface (fig. 3(a)) gave infra-red bands at 3750, 3670 and 3530 cm^{-1} and showed an intensity of absorption at *ca.* 1620 cm^{-1} slightly above that expected for bulk silica. The silica had retained a high surface concentration of adjacent hydrogen-bonding hydroxyl groups and also a small amount of molecular water.^{8, 9} Following adsorption strong infra-red bands, characteristic of diethylurea, appeared at 3340, 1635 and 1555 cm^{-1} (fig. 3(b)). Weak shoulders at 3140 and 3050 cm^{-1} are also due to the urea. No surface urethane was formed: the strong urethane band at 1697 cm^{-1} was absent. In the presence of excess ethyl isocyanate diethylurea was formed not only on the surface of the silica but also appeared as fine crystals on the walls of the infra-red cell. The compound was removed from the cell, recrystallized from ether, and its identity established by infra-red, n.m.r. and mass spectrometric methods. The melting point, and a mixed melting point with an authentic sample of 1,3-diethylurea, was 112°C (lit.¹⁰ 112°C).

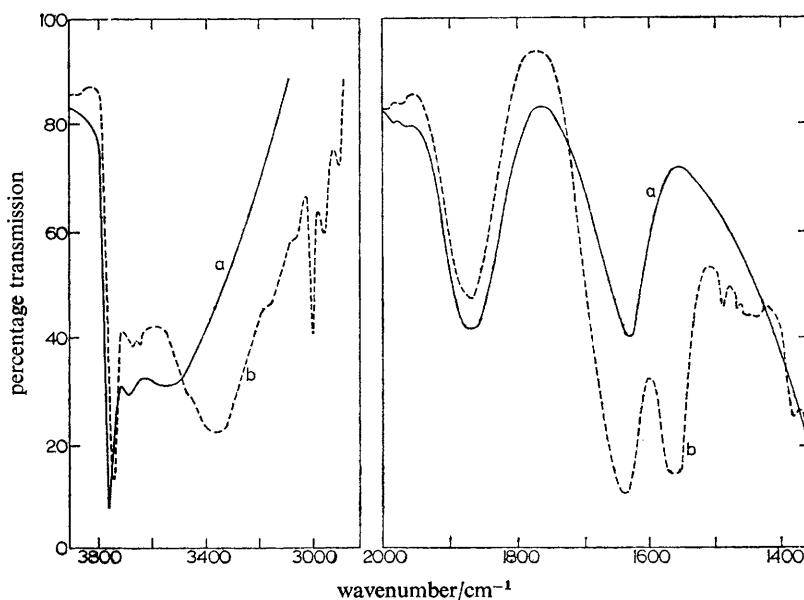


FIG. 3.—*a*, Silica exposed to water vapour (2.7 kN m^{-2} , $\frac{1}{2}$ h, 298 K) and evacuated (3 min, 298 K); *b*, after adsorption of ethyl isocyanate (2.4 kN m^{-2} , 10 h, 306 K) and evacuation (2 h, 306 K).

The effect of temperature on the adsorption products from ethyl isocyanate and silica is shown in fig. 4. The surface urethane was more easily removed than diethylurea by high temperature evacuation. The removal of the urethane was accompanied by a concomitant increase in the intensity of the band at 3750 cm^{-1} due to isolated hydroxyl groups. However, the restoration of the latter was not complete. The final optical density at 3750 cm^{-1} after the complete removal of urethane (fig. 4(d)) was 85 % of the value before adsorption of ethyl isocyanate. Mass spectrometric analysis of the desorption products showed that they consisted predominantly of ethyl isocyanate together with some carbon dioxide. The band at 3440 cm^{-1} remaining after evacuation at 573 K appears to be associated with the presence of diethylurea on the surface. The band also appeared following evacuation at temperatures $> 323 \text{ K}$ of the surface represented by the spectrum in (fig. 3(b)) which showed no

evidence for adsorbed urethane. Unperturbed NH groups in either the surface urethane or diethyl urea probably give rise to the band at 3440 cm^{-1} whereas NH groups perturbed by hydrogen-bonding give a broader band at *ca.* 3350 cm^{-1} .

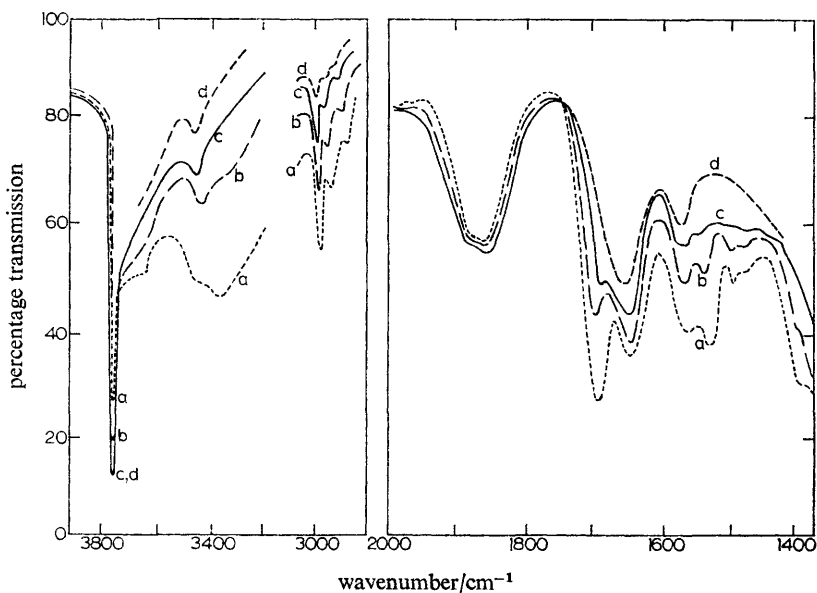
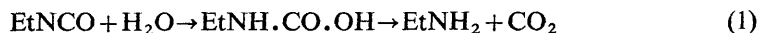


FIG. 4.—Desorption of adsorption products from silica by evacuation at (continued from fig. 1(e))
a, 334 K, 16 h; *b*, 391 K, 16 h; *c*, 481 K, 45 min; *d*, 573 K 18 h.

THE INFLUENCE OF SILICA ON THE REACTION BETWEEN WATER AND ETHYL ISOCYANATE

The observed copious formation of diethylurea which occurred when ethyl isocyanate adsorbed on a hydroxylated silica surface suggested that silica might be capable of promoting the hydrolysis reaction of ethyl isocyanate to ethylamine and hence to diethylurea. This was confirmed by the addition of silica to liquid mixtures of ethyl isocyanate and water.

Ethyl isocyanate and water are immiscible at room temperature and separate into two phases after shaking. On standing for 24 h a few crystals of diethylurea appeared. When the liquids were shaken in the presence of some aerosil silica the system acquired colloidal stability and did not separate into two distinct phases. On standing a high yield of diethylurea was obtained. At 303 K this occurred after approximately one hour. The yield of diethylurea depended on the molar ratio of ethyl isocyanate to water in the liquid mixture. With excess water carbon dioxide was evolved and ethylamine appeared as an oily liquid (reaction 1).



In the presence of higher proportions of ethyl isocyanate the ethylamine was able to react further (reaction 2)



to give the crystalline diethylurea as product.

THE REACTIONS OF ETHYL ISOCYANATE WITH SILICA AT HIGH TEMPERATURES

Silica was evacuated at 483 K and then reacted with ethyl isocyanate (4.7 kN m^{-2} , 16 h) at the same temperature. The infra-red spectrum was recorded after the sample was cooled and evacuated (306 K, 40 min). The absence of a band at 1555 cm^{-1} showed that there was no diethylurea on the surface. Some urethane may have been present although it is more likely that bands which were at 1530, 1660 and 1700 cm^{-1} are associated with the formation of the biuret $\text{EtNH}\cdot\text{CO}\cdot\text{NEt}\cdot\text{CO}\cdot\text{NHEt}$ or other reaction products from diethylurea and ethyl isocyanate. Biurets are formed by the reactions of ureas with isocyanates at temperatures $> ca. 373 \text{ K}$.² Bands due to the CH-stretching vibrations of ethyl groups ($2985, 2943, 2889 \text{ cm}^{-1}$) and the NH-stretching vibrations of perturbed (shoulder at $ca. 3380 \text{ cm}^{-1}$) and unperturbed (3450 cm^{-1}) NHet groups were also observed. The disappearance, on reaction with ethyl isocyanate, of the shoulder at $ca. 3680 \text{ cm}^{-1}$ in the spectrum of silica out-gassed at 483 K is consistent with the formation of diethylurea as a precursor of a biuret. A decrease in the intensity of the narrow band at 3750 cm^{-1} was accompanied by the appearance of a broader absorption maximum centred at 3680 cm^{-1} . The

latter band is tentatively assigned to —SiOH groups which are hydrogen bonded to the carbonyl groups of adjacent reaction products adsorbed on the surface. A band at 2308 cm^{-1} which resulted from the reaction at 483 K became more intense if the temperature of reaction was increased and was never present following reaction between silica and ethyl isocyanate at 306 K.

The reaction between silica and ethyl isocyanate at temperatures $\geq 573 \text{ K}$ led to the formation of negligible urethane, diethylurea or related products on the surface. As for reactions at lower temperature three main bands due to CH-stretching vibrations were present following reaction and evacuation at the high temperature. The most prominent infra-red bands due to adsorption products were at 2308 and 2210 cm^{-1} (fig. 5). The former appeared first (fig. 5(b, c)) but at higher coverages the latter also became intense (fig. 5(d)). The intensity of the maximum at 3750 cm^{-1}

due to —SiOH groups was hardly affected by the adsorption process and these groups were not therefore involved in the reactions. The positions and intensities of the bands at 2308 and 2210 cm^{-1} (and 2353 cm^{-1} , see below) were unaltered if ethyl isocyanate was reacted with a silica surface which had been predeuterated by exchange with deuterium oxide.

The effect of temperature on the desorption of the products of the high temperature reaction is exemplified in fig. 6. The band at 3750 cm^{-1} was unaffected by the desorption (except for decreases in intensity for the higher temperatures which occur even for pure silica) but the band at 3680 cm^{-1} (fig. 5(e)) diminished with increasing temperature and disappeared at 1118 K. A narrow band at 3500 cm^{-1} which appeared following evacuation at 773 K (cf. figs. 5(e) and 6(a)) was also removed at 1118 K. Of the two main products of adsorption the one responsible for the absorption maximum at 2308 cm^{-1} could be removed by evacuation at high temperatures but the species responsible for the maximum at 2210 cm^{-1} was thermally stable and could not be desorbed at temperatures up to 1218 K. The band however shifted to 2170 cm^{-1} . A shoulder at $ca. 2350 \text{ cm}^{-1}$ (fig. 5(d, e)) developed into a narrow band at 2353 cm^{-1} following evacuation at 873 K and higher temperatures but its intensity was considerably diminished by evacuation at 1218 K.

I.R. OF EtNCO ON SILICA

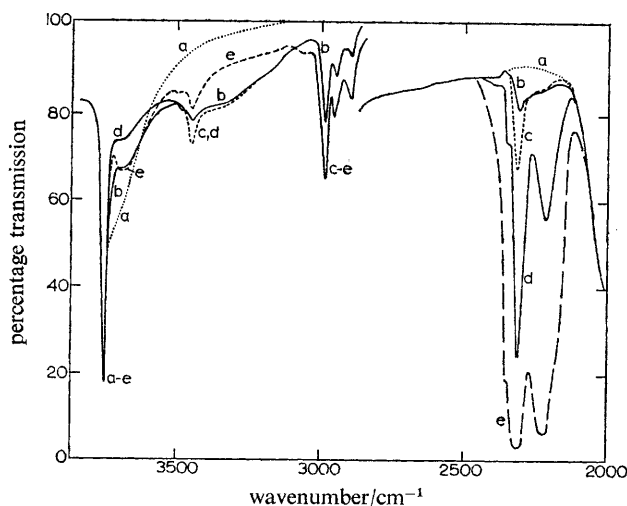


FIG. 5.—*a*, Silica after evacuation (673 K, 5 h). After exposure to ethyl isocyanate under the following conditions: *b*, 4 kN m⁻², 573 K, 1.8 h; *c*, 0.8 kN m⁻², 673 K, 1 h; *d*, 2.7 kN m⁻², 673 K, 1 h; *e*, 8 kN m⁻², 673 K, 12 h. Samples were evacuated at the reaction temperature for 45 min before cooling to 306 K for spectroscopic examination.

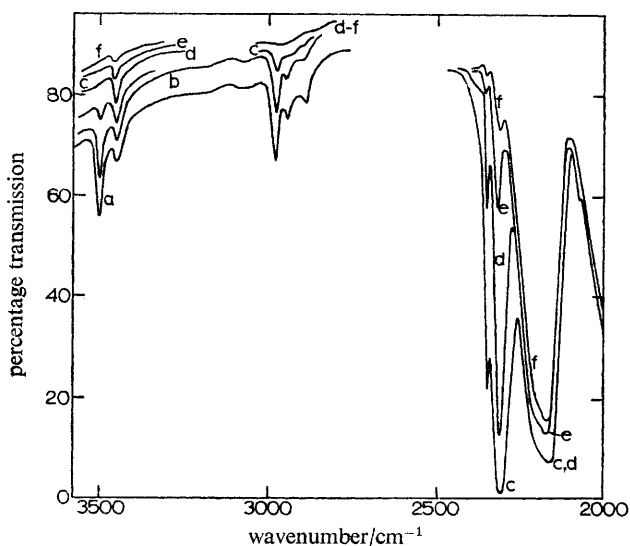


FIG. 6.—Desorption of the products of the high temperature reaction of ethyl isocyanate with silica (fig. 5(*e*)). Times and temperatures of evacuation were: *a*, 773 K, 30 min; *b*, 873 K, 30 min; *c*, 973 K, 30 min; *d*, 1118 K, 45 min; *e*, 1218 K, 20 min; *f*, 1218 K, 50 min.

The bands at 2308 and 2210 cm⁻¹ were both removed by hydrolysis with water vapour at 298 K (fig. 7). Their removal was accompanied by the appearance of bands at 1738 and 3430 cm⁻¹ and a shoulder at *ca.* 3520 cm⁻¹. These bands are consistent with the formation of an amide, probably formamide,¹¹ as a hydrolysis product. The absorption maximum at 2308 cm⁻¹ is assigned to isocyanate groups attached to silicon atoms in the oxide surface. This assignment is consistent with

the infra-red spectrum of silicon tetracyanate for which the strongest band at 2284 cm^{-1} has been attributed to the NCO pseudo anti-symmetric stretching vibration.¹² The band at 2210 cm^{-1} is due to cyanide groups possibly also attached to surface silicon atoms. Thus silyl cyanides exhibit a strong absorption maximum at *ca.* 2190 cm^{-1} .¹³ However, bands at 2220 cm^{-1} and 2200 cm^{-1} have been observed when hydrogen cyanide was adsorbed on silica¹⁴ and alumina¹⁵ respectively. The bands were assigned to cyanide groups in compounds formed by the polymerization of the adsorbate.

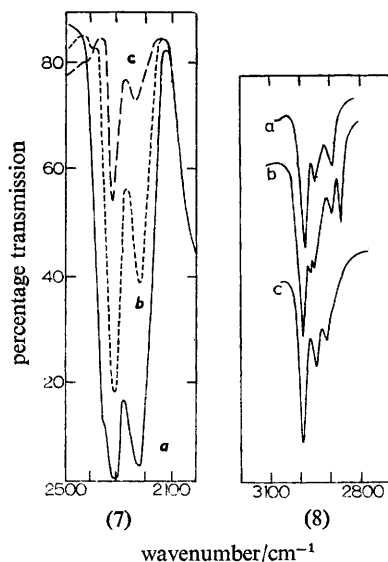


FIG. 7.—The hydrolysis of the products of reaction between silica and ethyl isocyanate at 673 K. *a*, Surface similarly treated to that represented by fig. 5(*e*); *b*, after contact with water vapour (2.7 kN m^{-2} , 298 K, 1 h); *c*, further hydrolysis (3.9 kN m^{-2} , 298 K, 4 h).

FIG. 8.—Effect of evacuation at high temperature on the CH-stretching region of the spectrum. *a*, Reaction and evacuation at 673 K (as fig. 5(*c-e*)); *b*, reaction (6.3 kN m^{-2} of ethyl isocyanate for 16 h) at 673 K followed by cooling to 306 K and subsequent evacuation at 306 K; *c*, silica evacuated at 1153 K for 20 min, exposed to ethanol vapour (2.3 kN m^{-2} , 306 K, 16 h) and evacuated at 306 K (20 min), 493 K (40 min), and finally 703 K (2 h).

In some cases studied two extra bands at 2860 and 2962 cm^{-1} (fig. 8(*b*)) were observed in the CH-stretching region of the spectrum. The bands appeared whenever the products of the high temperature adsorption were cooled to room temperature in the presence of ethyl isocyanate before evacuation. A typical spectrum is compared in fig. 8 with the result from a corresponding study in which reaction at high temperature was followed by evacuation at the high temperature before cooling. The presence of the bands at 2860 and 2962 cm^{-1} also coincided with a lower intensity of the band at 2210 cm^{-1} due to cyanide groups and a higher intensity of the band at *ca.* 1740 cm^{-1} which has been assigned to the carbonyl group stretching vibration of an amide. Methanol chemisorbs on silica to give surface —SiOMe groups which exhibit absorption maxima at 2859 and 2959 cm^{-1} .¹⁶ The present results suggest that these groups are formed in the high temperature reaction of ethyl isocyanate

with silica but that they are unstable to evacuation at high temperatures. It might be expected that —SiOEt groups are more likely to have been formed in the adsorption process. In order to test this point silica was exposed to ethanol at 306 K and subsequently evacuated at a series of increasing temperatures. The interaction between ethanol and silica was similar to that between methanol and silica.¹⁶ In the presence of ethanol vapour the band at 3750 cm^{-1} was perturbed by a hydrogen-bonding interaction. Desorption of hydrogen-bonded ethanol molecules left three absorption maxima at 2990 , 2945 and 2915 cm^{-1} (fig. 8(c)) due to ethanol chemisorbed as surface —SiOEt groups. The positions of the three bands were unchanged by evacuation at 306, 493 or 703 K. These results confirm that the three bands (fig. 8(a)) which result from the reaction of ethyl isocyanate and silica can, at least in part, be ascribed to the formation of ethoxy groups on the oxide surface.

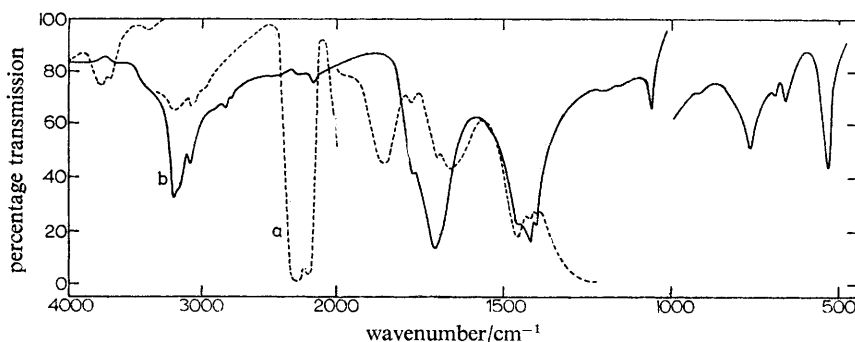


FIG. 9.—The formation of isocyanuric acid. *a*, Products of reaction of ethyl isocyanate (13.3 kN m^{-2}) and silica (830 K, 48 h) followed by evacuation (830 K, 30 min); *b*, product from the walls of the infra-red cell (pressed in a KBr disc).

Under conditions of extremely high temperature ethyl isocyanate forms hydrogen isocyanate as a pyrolysis product which polymerized on the surface of silica to give isocyanuric acid. A typical spectrum is shown in (fig. 9(a)). The isocyanuric acid also sublimed from the silica surface and collected on the cold walls of the infra-red cell. A spectrum (fig. 9(b)) of the compound taken from the cell walls corresponded closely to the published spectra^{17, 18} of isocyanuric acid. The most prominent bands observed here were at 3215 , 3090 , 2165 , 1775 , 1715 , 1465 , 1418 , 1405 , 1055 , 765 , 688 , 655 and 532 cm^{-1} . Assignments are given elsewhere.¹⁸ Deuteration produced new bands at 2390 , 2300 , 878 , 868 and 562 cm^{-1} which are close to recorded maxima¹⁸ for isocyanuric [^2H]acid.

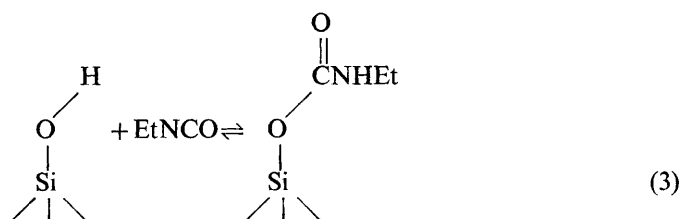
THE PYROLYSIS OF ETHYL ISOCYANATE

The reaction of ethyl isocyanate with silica at high temperatures produced a variety of adsorbed species some or all of which may have been formed by interactions between silica and the products of gas-phase pyrolysis of the isocyanate. The pyrolysis of ethyl isocyanate in the absence of silica was therefore briefly investigated. Heat treatment of the isocyanate ($0.8\text{--}2.6\text{ kN m}^{-2}$) had no effect below 673 K. At 750 K for one hour slight decomposition to hydrogen isocyanate, ethylene,

methane and hydrogen cyanide occurred. The extent of decomposition to these products was much greater at 913 K (1 h) at which temperature the greatest yield of hydrogen isocyanate was observed. At higher temperatures (1008 K) the hydrogen isocyanate was itself completely reacted, the main gas-phase products were hydrogen cyanide, methane, ethylene and carbon monoxide and an oily liquid appeared on the cold surfaces of the cell. The gas-phase products were identified by infra-red spectroscopy. Mass spectrometric analysis showed that hydrogen was also formed as a decomposition product.

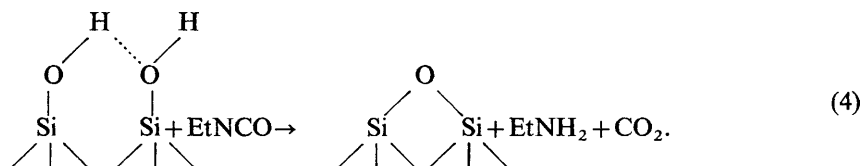
DISCUSSION

The products of adsorption or reaction of ethyl isocyanate on silica depend upon the temperature of reaction and the temperature at which the silica had been evacuated prior to reaction. Evacuation at 973 K followed by reaction at 306 K led to the formation of a urethane by reaction of surface silanol groups with the adsorbate. The overall reaction may be written as



although the exact mechanism of adsorption must be in doubt.¹⁹ The reversibility of the reaction was confirmed by the reappearance of the infra-red band at 3750 cm^{-1} and the presence of ethyl isocyanate as the predominant gas-phase product following evacuation at elevated temperatures and is consistent with the known decomposition reaction of urethanes to an isocyanate and a hydroxy compound.² In accord with the present results Kulik *et al.*³ have observed that butyl isocyanate adsorbs on silica to form a surface urethane which is stable to evacuation at 373 K but is desorbed at 453 K.

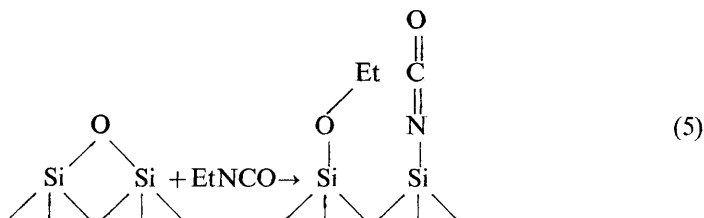
Molecular water adsorbed on silica reacts (eqn (1) and (2)) with ethyl isocyanate at 306 K to give 1,3-diethylurea which is probably formed on the oxide as a surface deposit. There is no evidence (fig. 3) for any chemisorptive interaction between diethylurea and the silica surface although some hydrogen bonding may occur. The silica is not necessarily catalytically active for the reaction between water and ethyl isocyanate despite its promotion of the reaction in the liquid phase. The formation of an emulsion of the two liquids in the presence of silica causes a large increase in the surface area of the liquid/liquid interface which would therefore favour an increased rate of reaction between the liquid components. The silica surface may also act in part as a catalyst for the reaction. Thus adjacent hydrogen bonded hydroxyl groups on the oxide surface must react with ethyl isocyanate as follows:



The ethylamine formed reacts rapidly¹ with a further molecule of ethyl isocyanate (reaction (2)). At the solid/vapour interface there was little or no molecular water

available to rehydroxylate the siloxane "bridges" and therefore the extent of diethyl-urea formation depended on the surface concentration of interacting hydroxyl groups. However at the solid/liquid interface rehydroxylation would occur and therefore allows reaction (4) to be repeated. There was no infra-red evidence for any reaction between ethyl isocyanate and siloxane "bridges" at 306 K.

The formation of negligible urethane when ethyl isocyanate reacts with silica at ≥ 573 K is consistent with the decomposition (reverse of reaction (3)) of surface urethane to ethyl isocyanate and silanol groups at high temperatures. The infra-red band at 3750 cm^{-1} was unaffected by the adsorption of ethyl isocyanate at 673 K. However, at high temperatures ethyl isocyanate is dissociatively chemisorbed on siloxane "bridges" according to reaction (5).



The reaction was reversed by evacuation at $>ca.$ 1000 K. The surface isocyanate group was responsible for the intense infra-red band at 2308 cm^{-1} and could be removed, initially as isocyanic acid, by hydrolysis with water vapour at 298 K. The dissociative chemisorption also apparently results in the formation of surface

---SiOMe (bands at 2860 and 2962 cm^{-1} : fig. 8(b)) and ---SiOH (band at 3680 cm^{-1} :

fig. 5(e)) groups which must arise from breakdown of the alkyl groups of the isocyanate molecules. The assignment of the infra-red band at 2210 cm^{-1} to cyanide group also implies that some breakdown of isocyanate groups occurs during adsorption. The decomposition reactions at 673 K depend upon the presence of the silica surface because no detectable decomposition occurred in the absence of silica at the same temperature. The band at 2210 cm^{-1} is analogous to similar bands observed when hydrogen cyanide adsorbs on alumina¹⁵ or on porous glass¹⁴ and assigned to the tetramer of HCN, diaminomaleionitrile. However, other reactions, including the

dissociative adsorption of HCN to give surface ---SiCN groups, also probably occur

and lead to a variety of related products.^{14, 15} The exposure of these cyano-compounds to water vapour would be expected to give amides, as observed, amongst the hydrolysis products.

The above discussion has emphasized the main features of the reactions of ethyl isocyanate and the surface of silica. At low temperatures isolated hydroxyl groups react to give a urethane whereas adjacent hydrogen-bonded hydroxyl groups and molecular water lead to the formation of diethyl urea. As the reaction temperature is raised these products are replaced by a biuret, dissociatively adsorbed isocyanate, cyanide, and ethoxy groups, and polymerization products including diaminomaleionitrile and isocyanuric acid. Many other products are probably formed in small proportions particularly at the higher temperatures and therefore a full analysis of all the observed infra-red bands has not been attempted. In most cases more than one of the main reactions occur simultaneously although by suitable choice of the reaction temperature and the pretreatment temperature of the silica a particular

reaction can sometimes become predominant. This is particularly so for the formation of a urethane by adsorption of ethyl isocyanate at 306 K onto silica previously evacuated at $>ca.$ 800 K.

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