J. Chem. Soc., Faraday Trans. 1, 1981, **77**, 1945-1952

Infrared Study of the Adsorption of Ethyl Isocyanate on Silica Immersed in Carbon Tetrachloride

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Received 27th August, 1980

Infrared spectra are reported of silica immersed in solutions of ethyl isocyanate in carbon tetrachloride. Interactions between surface silanol groups and ethyl isocyanate led to the formation of a surface urethane, ethylamine and 1,3-diethylurea as the products of adsorption. Increasing hydroxyl population of the silica surface enhanced the formation of 1,3-diethylurea but diminished the extent of reaction of isolated silanol groups to give urethane. Adsorbed ethylammonium ions were produced by proton transfer from silanol groups to ethylamine molecules at the solid/liquid interface. The results are discussed in relation to previous spectroscopic data for the adsorption of ethyl isocyanate on silica at the solid/vapour interface.

Reviews of the use of infrared spectroscopy for the study of adsorption behaviour at the solid/liquid interface have shown that spectra have been recorded for many classes of molecule adsorbed on silica immersed in carbon tetrachloride or liquid hydrocarbons.[1-3] The results have established that adsorption generally involves the formation of hydrogen bonds between surface silanol groups and functional groups in the adsorbate species. Adsorbed molecules retain their molecular identity and may be desorbed by replacement of the solutions in contact with the silica by pure solvent.

Infrared spectra characteristic of chemisorptive interactions at the silica/liquid interface have rarely been observed. In systems where the primary interactions involve the formation of hydrogen bonds, the spectral features due to vibrations of relatively small amounts of chemisorption products may be obscured and difficult to recognize. Molecules which are weakly adsorbed from the vapour phase may be easily desorbed by evacuation and therefore residual infrared bands due to vibrations of chemisorbed species are revealed. The corresponding procedure involving the solid/liquid interface is made difficult by the necessity to use a large volume of solvent and to keep the oxide immersed in liquid throughout the operation. Replacement of the solution surrounding silica discs by successive aliquots of pure solvent has been partially successful,[4] but is tedious because desorption may be slow.[5,6]

Infrared spectroscopy has established that proton transfer from surface silanol groups to aliphatic amines leads to an 'ion-pair' complex on silica immersed in carbon tetrachloride.[4] A further chemisorptive interaction between primary amines and surface siloxane groups led to secondary amino groups at the silica/liquid interface.[4,7] The present paper reports an investigation of the use of infrared spectroscopy for the characterization of chemisorptive interactions involving the surface of silica immersed in carbon tetrachloride. Ethyl isocyanate was chosen as adsorbate because its interaction with silica at the solid/vapour interface had been previously studied by infrared spectroscopy.[8]

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EXPERIMENTAL

The infrared cell[9] and procedures for the recording of infrared spectra[10] of pressed discs of silica (surface area, 176 m^2 g^{-1}) immersed in solutions of ethyl isocyanate in carbon tetrachloride have been described before. Ethyl isocyanate was purified by cold distillation and dried over type 4 A molecular sieve. Solutions of ethyl isocyanate in carbon tetrachloride were stored under nitrogen in a burette which was glassblown to the liquid inlet system of the infrared cell. The silica was taken from the same batch as had previously been used[8] in a study of the interactions between silica and ethyl isocyanate vapour.

RESULTS

ADSORPTION ON SILICA PREHEATED AT 943 K

Spectra of silica which had been preheated at 943 K exhibited a maximum at 3745 cm^{-1} [fig. 1 (*a*)] which shifted to 3686 cm^{-1} when the discs were immersed in carbon tetrachloride [fig. 1 (*b*)] and is due to the OH-stretching vibrations of isolated surface silanol groups. A negligible surface concentration of adjacent interacting silanol groups (bands at 3660 and 3550 cm^{-1})[11] remained after the heat treatment. The addition of ethyl isocyanate caused changes of the spectrum with time which were considerably slower [fig. 1 (*c*)-(*g*)] than the rates of equilibration previously observed,[11, 12] using the same apparatus and procedures, for systems in which only hydrogen-bonding interactions occurred at the solid/liquid interface. Chemisorptive interactions between ethyl isocyanate in solution and the silica surface were measurably slow.

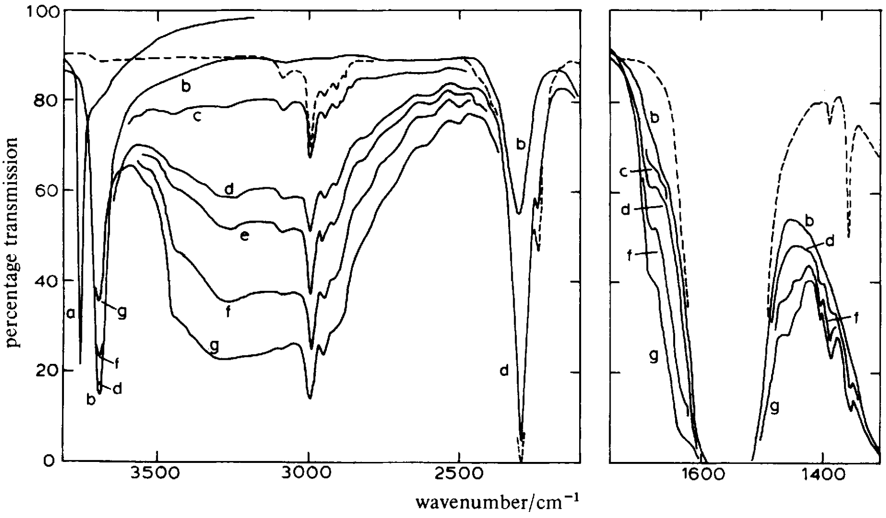


FIG. 1.—Spectra of silica (*a*) in vacuum after heat treatment (1.3×10^{-4} N m^{-2}, 943 K, 12 h), (*b*) in carbon tetrachloride, (*c*)-(*g*) in carbon tetrachloride containing ethyl isocyanate at concentrations/mmol dm^{-3} of 5.6 (after 1 h), 5.6 (19 h), 10.6 (1 h), 10.6 (5.5 h) and 10.6 (23 h), respectively. Dashed spectrum: solution of ethyl isocyanate (10.6 mmol dm^{-3}).

Decreases in the intensity of the maximum at 3686 cm^{-1} were accompanied by the appearance of a broad band envelope containing several maxima in the spectral range 2500-3600 cm^{-1} [fig. 1 (*c*)-(*g*)]. Bands at 3080, 2988, 2942, 2900 and *ca.* 2880 cm^{-1} were also present in spectra of ethyl isocyanate in solution (fig. 1) and may be assigned to

CH-stretching vibrations, primarily of ethyl isocyanate in solutions surrounding the disc. The band at 2988 cm^{-1} was apparently more intense than expected if it had been due solely to molecules in solution and therefore some contribution to the intensity of the band must be attributed to a CH-stretching vibration of alkyl groups in adsorbed species. The other bands were too weak to allow an assessment of possible contributions from surface species to be made. A broad maximum at 3270 cm^{-1} together with recognizable shoulders at 3440 and *ca.* 3380 cm^{-1} were absent from spectra of solutions in equilibrium with the disc and were in the spectral region typically containing maxima due to NH- or OH-stretching vibrations. Shoulders at 2810, 2710, 2610 and 2505 cm^{-1} were also absent from solution spectra and must have been due to vibrations of chemisorbed species.

Maxima at 2288, 2236, 1467, 1457, 1435, 1403, 1388 and 1353 cm^{-1} were present in spectra of both ethyl isocyanate in solution and of silica immersed in solutions of ethyl isocyanate (fig. 1). The intensities of the bands at 1467, 1457, 1435, 1403 and 1388 cm^{-1} were such that the maxima must have contained contributions due to vibrations of adsorbed species. The most prominent bands at 1467, 1457 and 1388 cm^{-1} may be assigned to CH-bending vibrations of alkyl groups. The intensities of the maxima at 2288 and 2236 cm^{-1}, assigned to the asymmetric vibration of the $N{=}C{=}O$ group,[13] could apparently be ascribed entirely to ethyl isocyanate in solution. The combined maxima were intense and the possibility of a small contribution from vibrations of adsorbed species cannot be discounted. However, the weaker band at 1353 cm^{-1} due to the symmetric vibration of the $N{=}C{=}O$ group[13] was of similar intensity for a particular solution concentration of ethyl isocyanate in the presence and absence of silica. Few, if any, isocyanate groups retained their integrity when ethyl isocyanate was adsorbed on silica at the solid/liquid interface.

The products of chemisorption of ethyl isocyanate on silica gave infrared bands at 1683 and 1630 (sh) cm^{-1} [fig. 1(*f*) and (*g*)] which were absent from spectra of ethyl isocyanate in solution. Corresponding maxima at 1697 and 1635 cm^{-1} in spectra of ethyl isocyanate adsorbed on silica at the solid/vapour interface were assigned to ($C{=}O$)-stretching vibrations of surface species.[8]

Spectra [fig. 2(*b*)] of the products of adsorption of ethyl isocyanate on silica in carbon tetrachloride were recorded after the concentration of ethyl isocyanate in solution had been reduced to zero [fig. 2(*d*)]. This was achieved by repeated replacement of the solution surrounding the silica disc by pure solvent until the spectrum of ethyl isocyanate in the liquid phase could not be detected. The disc remained immersed in liquid throughout the replacement procedure. The resulting spectrum of species at the solid/liquid interface exhibited no detectable bands in the spectral range 2200-2400 cm^{-1}. No isocyanate groups were present on the silica surface. Maxima were observed, however, at 2988, 2942, 2910 and 2890 cm^{-1}, assigned to CH-stretching vibrations, and at 1467, 1457 and 1388 cm^{-1} due to CH-bending vibrations of alkyl-containing adsorption products. The broad maximum at 3270 cm^{-1} [fig. 2(*b*)] showed no distinctive features but retained a shoulder at *ca.* 3440 cm^{-1}. Evidence also remained for shoulders at 2710, 2610 and 2505 cm^{-1}.

The adsorption of amines on silica immersed in carbon tetrachloride leads to the appearance in the spectral range 2450-2750 cm^{-1} of similar progressions of bands which have been assigned to NH-stretching vibrations of substituted ammonium ions.[4, 14] Infrared spectra of quaternary ammonium salts in KBr discs and of mixtures of amines and hydrogen chloride adsorbed on silica at the solid/vapour interface have confirmed these assignments.[15]

Shoulders at *ca.* 1683 and 1630 cm^{-1} remained in the spectra of the discs after removal of ethyl isocyanate from the solution. However, the 1500-1600 cm^{-1} region

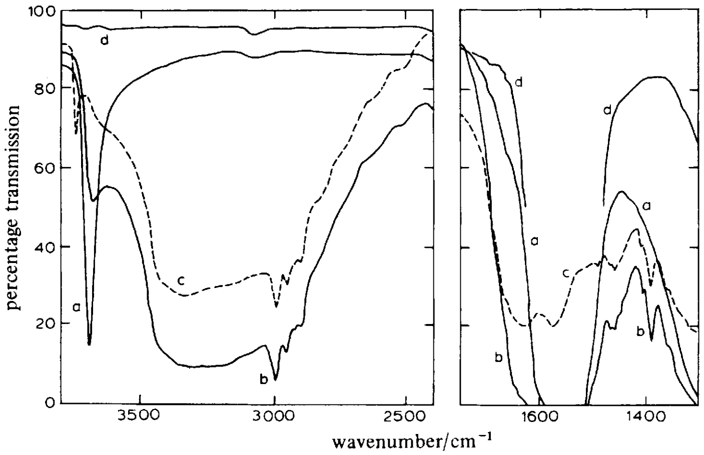


FIG. 2.—Spectra of silica after (*a*) evacuation (1.3×10^{-4} N m^{-2}, 943 K, 12 h) and immersion in carbon tetrachloride, (*b*) immersion in carbon tetrachloride containing ethyl isocyanate (10.6 mmol dm^{-3}, *ca.* 48 h) followed by repeated washing with pure carbon tetrachloride until the liquid phase in contact with the disc gave spectrum (*d*), (*c*) subsequent evacuation at beam temperature (17 min).

of the spectrum was obscured by an intense maximum resulting from vibrations of solvent molecules. This region was explored by drainage and evacuation of the infrared cell. Maxima at 1570 and 1630 cm^{-1} were revealed together with a scarcely discernible shoulder at *ca.* 1695 cm^{-1} [fig. 2(*c*)]. The attempts to desorb ethyl isocyanate from the silica surface failed to return the infrared band due to isolated silanol groups to its original intensity before adsorption took place (fig. 2). Isolated surface silanol groups had either reacted with ethyl isocyanate to form chemisorbed products or were perturbed by lateral interactions with chemisorbed species on adjacent surface sites.

ADSORPTION ON SILICA PREHEATED AT 433 K

Silica which had been preheated at 433 K gave infrared bands at 3745 cm^{-1} due to isolated silanol groups and at 3670(sh) and 3570(sh) cm^{-1} due to two types of adjacent interacting surface silanol groups [fig. 3(*a*)].[16] Immersion of silica in carbon tetrachloride gave a spectrum with a band at 3686 cm^{-1} and a shoulder at *ca.* 3500 cm^{-1} [fig. 3(*b*)]. Subsequent addition of ethyl isocyanate resulted in the appearance of absorption maxima which were at similar positions in the spectrum to the corresponding maxima for ethyl isocyanate adsorbed on silica which had been preheated at 943 K. The rate of adsorption was again slow (fig. 3) but the enhanced intensities of infrared bands due to adsorbed species for a particular added solution concentration of ethyl isocyanate suggested that a greater number of surface sites were involved in the chemisorptive interactions.

A maximum at 3440 cm^{-1} was more prominent [fig. 3(*d*)] in spectra of silica which had been preheated at 433 K than for silica which had been more extensively dehydroxylated (fig. 1). In contrast, the infrared bands in the range 2450-2750 cm^{-1} were less evident for the more hydroxylated silica. Contrasting behaviour was also observed for the shoulders at *ca.* 1683 and 1630 cm^{-1} which were less and more intense, respectively, for silica with a higher initial surface hydroxyl concentration. A similar effect has been reported[8] for the interaction between silica and ethyl isocyanate vapour. Prominent infrared bands at 3340, 1635 and 1555 cm^{-1} were assigned to vibrations of 1,3-diethylurea, the formation of which as a product of

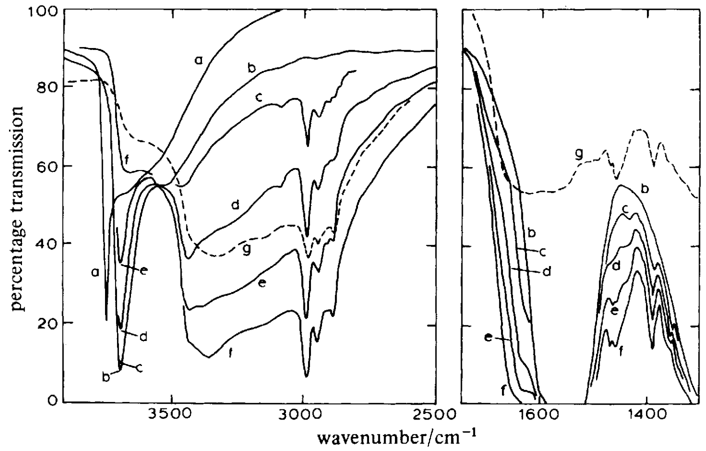


FIG. 3.—Spectra of silica (*a*) in vacuum after heat treatment (1.3×10^{-4} N m^{-2}, 433 K, 19 h), (*b*) in carbon tetrachloride, (*c*)-(*f*) after immersion in ethyl isocyanate solution (4.5 mmol dm^{-3}) for 5 min, 2 h, 6 h and 21 h, respectively, (*g*) after subsequent evacuation at beam temperature (30 min).

chemisorption was enhanced by increasing hydroxyl group population of the silica surface.[8] The corresponding enhancement of the maximum at 1630 cm^{-1} in the present study was accompanied by the increased prominence of a maximum at 3350 cm^{-1} [fig. 3(*f*)] which may be assigned to the NH-stretching vibration of 1,3-diethylurea formed as an adsorption product. A band at 1580 cm^{-1} was revealed [fig. 3(*g*)] following the removal of carbon tetrachloride by drainage and evacuation. The non-existence of surface isocyanate species was evidenced by the absence of infrared bands in the range 2200-2400 cm^{-1}.

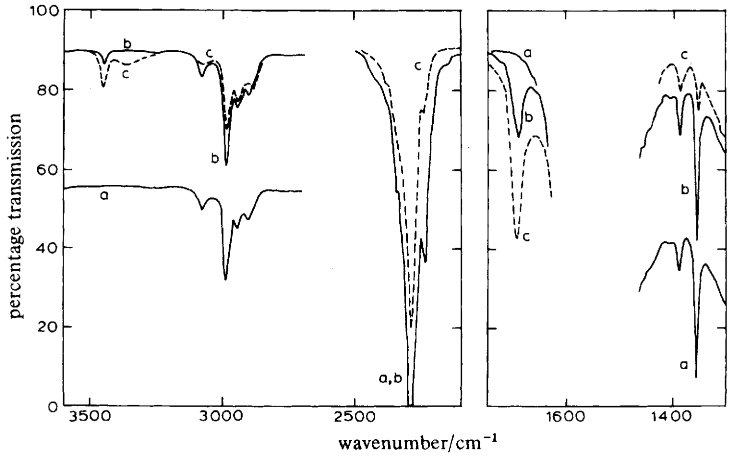


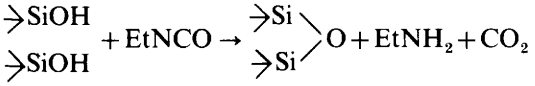
FIG. 4.—Spectra of (*a*) ethyl isocyanate in carbon tetrachloride (partially staggered for clarity), (*b*) liquid phase containing ethyl isocyanate (initially 4.5 mmol dm^{-3}) after contact with silica for 48 h and addition of further ethyl isocyanate (13.5 mmol dm^{-3}) immediately before spectrum recorded, (*c*) same solution after 72 h further contact with silica.

Spectra of solutions of ethyl isocyanate in contact with silica which had been preheated at 433 K underwent changes with time which may be ascribed to the formation of desorbed reaction products. Bands at 2288 and 1353 cm^{-1}, assigned to the asymmetric and symmetric stretching vibrations, respectively, of (N=C=O) groups, slowly decreased in intensity. New maxima simultaneously appeared at 3445, 3360 and 1693 cm^{-1} (fig. 4). A catalytic reaction involving the surface of silica gave products apparently containing NH (bands at 3445 and 3360 cm^{-1}) and C=O (1693 cm^{-1}) groups. No such reaction was evident when ethyl isocyanate solutions were contacted with silica which had been partially dehydroxylated by heat treatment at 943 K.

DISCUSSION

Infrared spectra of n-butyl[17-19] and ethyl[8] isocyanates adsorbed on silica at the solid/gas interface are complex and have been interpreted in terms of the generation of a variety of adsorption products or surface species. Predominant amongst these are a surface urethane[8, 17-19] formed by reaction (1) (R = Et or n-Bu), 1,3-diethylurea[8] formed *via* ethylamine in accordance with reactions (2) and (3), and tri-n-butyl isocyanurate,[19] a cyclic trimer of ethyl isocyanate.

$$\succ SiOH + RNCO \rightarrow \succ SiO\cdot CO\cdot NHR \qquad (1)$$



$$\begin{matrix}\succ SiOH\\ \succ SiOH\end{matrix} + EtNCO \rightarrow \begin{matrix}\succ Si\\ \succ Si\end{matrix}\!\!\!>\!O + EtNH_2 + CO_2 \qquad (2)$$

$$EtNH_2 + EtNCO \rightarrow EtNH\cdot CO\cdot NHEt \qquad (3)$$

Surface isocyanate and alkoxy groups have also been characterized.[8, 19] Products of the adsorption of ethyl isocyanate on silica immersed in carbon tetrachloride are difficult to identify with certainty for two reasons. First, many bands due to OH, NH and CH-stretching vibrations of surface species appeared in the spectral range 2500-3600 cm^{-1} and merged into an overall band envelope from which the precise positions, or even the existence, of many bands could not be unambiguously discerned. Secondly, the intense absorption maximum at 1500-1600 cm^{-1} in the spectrum of liquid carbon tetrachloride obscured a spectral region in which maxima due to characteristic vibrations of expected reaction products would have occurred. The band was too intense for solvent blanking to be effective. However, similarities which exist between the spectroscopic results for the adsorption of ethyl isocyanate on silica at the solid/vapour[8] and solid/liquid interfaces have helped in the interpretation of the present data.

Eley *et al.*[8] provided unequivocal evidence for the formation of 1,3-diethylurea when ethyl isocyanate vapour interacted with the surface of silica at *ca.* 306 K. Infrared bands at 3340, 1635 and 1555 cm^{-1} due to vibrations of adsorbed 1,3-diethylurea were compared with corresponding maxima at 3350, 1635 and 1574 cm^{-1} in spectra of solutions of 1,3-diethylurea in carbon tetrachloride. Maxima at 3350, 1630 and 1570-80 cm^{-1} in the present spectra are similarly ascribed to the formation of 1,3-diethylurea as an adsorption product. The greater prominence of the maxima at 3350 and 1630 cm^{-1} for silica which had been preheated at 433 K rather than 943 K is in accordance with the observation that the formation of 1,3-diethylurea at the solid/vapour interface became more favourable with decreasing pretreatment temperature of the silica adsorbent. The implication that physisorbed molecular water is a necessary ingredient for the formation of 1,3-diethylurea[19] is incorrect. Chemisorbed water in the form of neighbouring surface silanol groups has been proposed[8] as the active species responsible for the hydrolysis of ethyl isocyanate to ethylamine [reaction (2)], which is the precursor of 1,3-diethylurea [reaction (3)].

Maxima at 1697 and 1525 cm^{-1} have been assigned to the (C=O)-stretching and NH-deformation vibrations, respectively, of a surface urethane formed by the reaction of ethyl isocyanate vapour with isolated surface silanol groups on silica [reaction (1)].[8]

Maxima at 1700 or 1670 cm^{-1} and 1540 or 1560 cm^{-1} in spectra of n-butyl isocyanate adsorbed on silica have been similarly assigned.[17-19] The band in the present spectra at 1683 cm^{-1} (fig. 1) is attributed to the formation of surface urethane at the silica/carbon tetrachloride interface. The possible existence of the second band was obscured by the intense maximum due to solvent. However, removal of the liquid phase caused the appearance of a weak shoulder at 1520 cm^{-1} [fig. 2(*c*) and 3(*g*)] which can tentatively be assigned to the NH-deformation vibration of surface urethane.

Increasing dehydroxylation of the silica surface before the admission of ethyl isocyanate enhanced the extent of formation of surface urethane both at the solid/vapour and the solid/liquid interfaces. Silica which had been preheated at 973 K interacted with ethyl isocyanate vapour to give a surface urethane, but no 1,3-diethylurea.[8] The presence of isolated surface silanol groups (band at 3745 cm^{-1}) favoured the formation of urethane and the absence of adjacent interacting silanol groups precluded the formation of 1,3-diethylurea. In contrast, the adsorption of ethyl isocyanate on silica which was heated at 943 K before immersion in carbon tetrachloride resulted in the generation of less surface urethane than appeared in the equivalent reaction at the solid/vapour interface, but gave an appreciable amount of 1,3-diethylurea (fig. 2). The formation of each 1,3-diethylurea molecule would have required the participation of the elements of water derived from two isolated surface silanol groups which would have been too far apart to interact simultaneously with a single adsorbate molecule. The presence of liquid carbon tetrachloride in contact with silica apparently promotes the mobility of surface species, possibly protons, and therefore enhances the probability either that two protons will exist simultaneously at a reaction site or that a second proton may arrive at a site at which reaction involving a first proton has already taken place.

Ethylamine would be expected to be an intermediate in the formation of 1,3-diethylurea from ethyl isocyanate [reactions (2) and (3)]. The existence of bands in the present spectra (fig. 1) at 3440 (sh), 3270, 2810 (sh) 2710 (sh), 2610 (sh) and 2505 (sh) cm^{-1} may be compared with infrared spectra of butylamines adsorbed on silica immersed in carbon tetrachloride.[4] Tri-n-butylamine, di-n-butylamine and n-butylamine gave maxima at 3270, 3230 and 3280 cm^{-1}, respectively, at high surface coverages with spectra of the adsorbed primary amine also exhibiting a shoulder at 3440 cm^{-1}. Bands at 2730, 2640 and 2530 cm^{-1} in spectra of tri-n-butylamine on silica were assigned to NH-stretching vibrations of NH^+-groups formed by proton transfer from isolated surface silanol groups to adsorbed amine molecules. Corresponding bands were at 2640 (sh) and 2530 cm^{-1} in spectra of n-butylamine on silica. Maxima at 2740, 2630 and 2530 cm^{-1} have been recorded in spectra of n-butylammonium ions formed by the co-adsorption of n-butylamine and hydrogen chloride on silica at the solid/vapour interface.[15] The spectra of ethyl isocyanate on silica therefore provide strong evidence for the existence of ethylamine, not only as an intermediate in the formation of 1,3-diethylurea, but also as a surface species present in detectable amounts. The protonation of ethylamine molecules at the solid/liquid interface contrasts with the mode of adsorption of aliphatic amines on silica at the solid/vapour interface[20] for which only hydrogen-bonding interactions can be detected by infrared spectroscopy. The Brønsted acidity of isolated surface silanol groups is apparently enhanced by the immersion of silica in carbon tetrachloride. Enhanced proton mobility at the solid/liquid interface may be responsible for the appearance of ethylamine and 1,3-diethylurea as chemisorption products on silica which had been preheated at 943 K. Neither product was formed at the solid/vapour interface on silica which had been preheated at 973 K. The shoulder at 2810 cm^{-1} in spectra of ethyl isocyanate on silica in carbon tetrachloride is comparable with a band at 2805 cm^{-1}.

in spectra of adsorbed n-butylamine.[4] The band was attributed to the formation of a secondary amine species by chemisorption of n-butylamine onto siloxane groups in the silica surface.

Guillet *et al.*[19] have presented evidence for the existence of isocyanate groups on silica at the solid/vapour interface after adsorption of n-butyl isocyanate at ambient temperatures and desorption at 373, 473 or 573 K. Eley *et al.*[8] reported the formation of chemisorbed isocyanate groups when ethyl isocyanate vapour interacted with silica at high temperatures, but not at *ca.* 306 K. The absence of spectroscopic evidence for chemisorbed isocyanate groups on silica after the adsorption of ethyl isocyanate from solution in carbon tetrachloride at *ca.* 300 K is therefore consistent with our previous results[8] for the corresponding process at the solid/vapour interface.

A possible assignment of the band at 1693 cm^{-1} which developed in spectra (fig. 4) of solutions of ethyl isocyanate in contact with silica would be that the band results from the (C=O)-stretching vibrations of triethyl isocyanurate formed by trimerization of ethyl isocyanate.[19] However, the concomitant appearance of maxima at 3445 and 3360 cm^{-1} suggests that secondary amido (CO·NHEt)-groups[21, 22] were also present in the desorbed reaction products. Slow oligomerization of ethyl isocyanate gave a cyclic trimer containing no hydrogen atoms other than those in ethyl groups and linear oligomers containing CO·NHEt end groups with hydrogen atoms derived from the silica surface.

We thank Tioxide International Ltd for the award of a Studentship (S.N.W.C.).

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