

21 700  $\text{cm}^{-1}$ , while the corresponding values for psoralene are 6000 and 21 600  $\text{cm}^{-1}$ . Table 2 gives the transition energies  $\Delta E$  and  $\lambda_{\text{max}}$  calculated via  $\nu_0 = 5300 \text{ cm}^{-1}$ ,  $\beta_0 = 21 700 \text{ cm}^{-1}$  for the coumarins and  $\nu_0 = 6000 \text{ cm}^{-1}$ ,  $\beta_0 = 21 600 \text{ cm}^{-1}$  for the furocoumarins; Figs. 1 and 2 show the spectra in cyclohexane and alcohol,\* with the theoretical spectra indicated by lines at the bottom. The Hückel approximation gives a generally satisfactory prediction of the main bands, the agreement being better for the end bands than for the middle ones.\*\*

Although the intensity calculations for coumarin and psoralene show that all the transitions are allowed the actual values (Table 3) do not agree with experiment. This is not unexpected and is a result of the assumptions made in the calculations.

We are indebted to A. V. Tutkevich for providing the program for the calculations and to N. P. Gambaryan for discussion of several aspects.

\*Spectra recorded with an SF-4 spectrophotometer.

\*\*It should be remembered that overlap of the bands can cause the maxima to be displaced.

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#### KINETICS OF ISOTOPE EXCHANGE BETWEEN HCl AND DBr IN LIQUID NITROGEN AND OXYGEN

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Not much is known about hydrogen isotope exchange when the protons are linked to atoms with nonbonding electron pairs. NMR provides considerable scope for research in this area [1-4], but almost all papers on this deal with pure liquids or binary mixtures of these, whereas, as regards mechanisms, it is of most interest to examine processes in vapors or in solution in solvents free from active hydrogen. Studies of exchange at low temperatures should also provide useful evidence.

The present solvents were chosen as being highly transparent in the infrared [5], so, even though the hydrogen halides have solubilities of only  $10^{-4}$  to  $10^{-3}$  M, the absorption spectra of HCl and DBr should be accessible with layers of usable thickness. The processes may be followed by reference to the intensities of the  $\nu(\text{HCl})$ ,  $\nu(\text{HBr})$ ,  $\nu(\text{DCl})$ ,  $\nu(\text{DBr})$  bands as functions of time.

#### EXPERIMENTAL

We used an IKS-12 spectrometer with an LiF prism and OAP-1 Golay detector. The spectral slit width was 7-8  $\text{cm}^{-1}$ . The solutions of HCl and DBr were prepared by mixing the solid halide with the solvent and allowing the mixture to stand for several hours with periodic stirring, followed by filtration. The first measurements were made with the cell described in [5]. A layer 6 cm thick was inadequate to reveal the absorption band of DBr in saturated solution, so a simple double-pass cell was made, which raised the effective path length to 40 cm (Fig. 1). This cell was based on a glass dewar having at the bottom a steel concave spherical mirror of radius of curvature 20 cm. Entry of water into the solution (which causes strong scattering and also a broad band at 2900-3200  $\text{cm}^{-1}$ ) was prevented by a 10  $\mu\text{m}$  teflon film, which does not absorb in the region of interest. A 35 cm path showed  $\nu(\text{DBr})$  as a peak at about 1830  $\text{cm}^{-1}$ ;  $\nu(\text{HCl})$  was much stronger and could be detected at smaller thicknesses. Addition of pure solvent did not affect the intensity, so Beer's law applies at the concentrations used. The signal was affected by the displacement of the image of the source along the axis when the layer thickness was altered from 7 to 40 cm. The saturated solutions of HCl and

DBr (isotopic abundance of D in the latter about 90%) in liquid nitrogen were mixed in roughly a 1:10 ratio, and the spectrum over the range covering  $\nu(\text{HCl})$ ,  $\nu(\text{HBr})$ ,  $\nu(\text{DCl})$ ,  $\nu(\text{DBr})$  was recorded for several hours; the liquid level changed by only 3–4 cm in 5 hr.

## RESULTS AND DISCUSSION

The absorption bands of DBr, DCl, and HCl lie clear of the solvent absorption, but  $\nu(\text{HBr})$  lies in a region where nitrogen absorbs weakly (Fig. 2). The conditions of observation are less favorable with liquid oxygen; Fig. 3 shows that all the bands are overlapped to some extent by absorption due to the oxygen or to impurities in it [5]. However, it was possible to make quantitative measurements on  $\nu(\text{HCl})$  and  $\nu(\text{DCl})$ .

The strengths of the bands  $\nu(\text{HCl})$ ,  $\nu(\text{DBr})$ , and  $\nu(\text{HBr})$  did not alter immediately after mixing, while  $\nu(\text{DCl})$  was absent. Within 5–10 hr there were appreciable falls in  $\nu(\text{DBr})$  and  $\nu(\text{HCl})$ , while  $\nu(\text{DCl})$  appeared, and the strength of  $\nu(\text{HBr})$  increased.

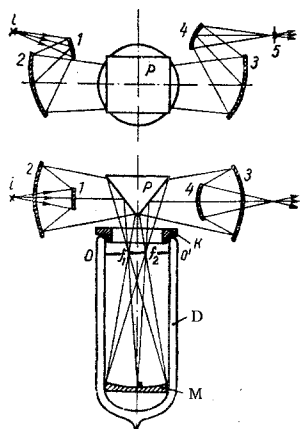


Fig. 1. Double-pass cell: i—light source, P—prism, D—dewar, M—spherical mirror, K—holder with teflon film, OO'—liquid level,  $f_1$  and  $f_2$ —intermediate images of source, 1–4) mirrors in illumination system.

The results give upper limits for the exchange rate constants at 77 and 90° K. The concentrations were deduced from published values for the integral absorption coefficients  $A$  of  $\nu(\text{HCl})$ ,  $\nu(\text{HBr})$ , and  $\nu(\text{DCl})$ ; that for  $\nu(\text{HCl})$  in the vapor state at room temperature is 3000 l/mole · cm<sup>2</sup> [6] but in a mixture with nitrogen under high pressure at –80° C it is 4500 [7], the coefficient increasing with the nitrogen pressure and as the temperature is reduced. In  $\text{CCl}_4$  at room temperature, the value is 7500 [8], while in crystalline HCl it is 22 500 [9]. For HCl dissolved in these liquids we took  $A = 7500$ , which cannot differ from the true value by more than a factor two. This value was used to determine the HCl concentrations in liquid nitrogen from

$$c = \frac{2.3}{l} \frac{\int \lg(I_0/I) dv}{A}$$

Spectra of solutions with concentrations measured in this way were used to determine the absorption coefficient at the peak of the  $\nu(\text{HCl})$  band, which is more

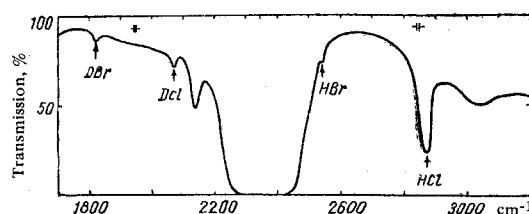


Fig. 2. Transmission of liquid nitrogen containing dissolved HCl, HBr, DCl, and DBr (effective layer thickness 38 cm).

convenient than  $A$  if the recording conditions are standardized. The concentrations of HBr and DCl in liquid nitrogen were deduced from the integral absorption coefficients in  $\text{CCl}_4$  at room temperature [8]. As  $A/\nu^2$  is invariant under isotope substitution for unperturbed diatomic molecules [10], we can use  $A_{\text{HBr}}$  to calculate  $A_{\text{DBr}}$ . In fact,  $A/\nu^2$  changes only 10% [8] between HCl and DCl in  $\text{CCl}_4$ . Taking the ratio of the  $A/\nu^2$  for HBr and DBr as being as for HCl and DCl dissolved in  $\text{CCl}_4$ , we get the  $A$  for DBr in  $\text{CCl}_4$  as 2200, which was used for the solutions in liquid nitrogen and oxygen. The HCl concentration in the kinetic tests was 0.2–0.3 mM, while the total content of both isotopic forms of hydrogen bromide was 0.05–0.1 M.

The concentration of each component tends exponentially to its equilibrium value [11]. The exponent  $r < 10^{-4} \text{ sec}^{-1}$ , so, if the reaction is assumed bimolecular, the upper limit to the rate constant can be determined at 77° and 90° K,

$$k_{77^\circ} = \frac{r}{[\text{HCl}] + [\text{DBr}] + [\text{HBr}]} < 0.1 \text{ l/mole} \cdot \text{sec}$$

HCl and DBr in  $\text{CCl}_4$  at room temperature come to equilibrium in less than 5 sec, so

$$k_{300^\circ} > 10^2 \text{ l/mole} \cdot \text{sec}.$$

These results indicate (Fig. 4) that  $E_a > 1.5 \text{ kcal/mole}$ .

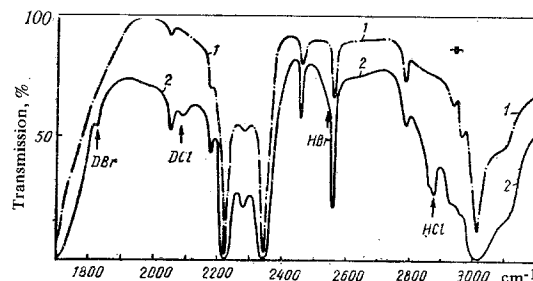


Fig. 3. 1) Transmission of liquid oxygen (effective layer thickness 12 cm); 2) transmission of liquid oxygen containing dissolved HCl, HBr, DCl, and DBr (effective layer thickness 40 cm).

The activation energy for viscous flow of liquid nitrogen, as deduced from Eyring's formula [12] via data on the temperature dependence of the viscosity [13] and density [14], is 0.66 kcal/mole; Frenkel [15]

gives the similar value of 0.47 kcal/mole, and both are much less than the above lower limit for  $E_a$ . There is therefore little doubt that this is a reasonable estimate of the true value.

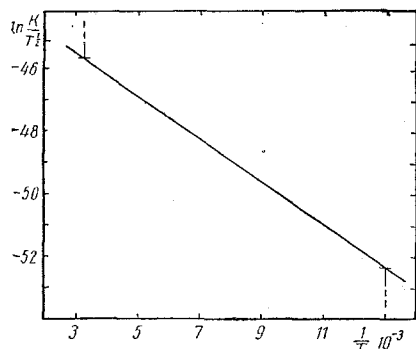


Fig. 4. Estimation of the lower limit to the activation energy for hydrogen exchange in HCl + DBr.

The result  $E_a > 1.5$  kcal/mole gives some indication of the rate-limiting step. It has been shown [16] from the generally accepted mechanism [17] that, if this step is decay of a hydrogen-bonded complex in which proton exchange occurs [18], then the temperature dependence of the rate constant will be determined by the factor  $\exp(\delta/RT)$ , in which  $\delta$  is the activation energy for formation of that complex. This  $\delta$  should be almost zero; it can hardly be greater than the  $\delta$  for formation of a complex of donor-acceptor type, and it is known [19] that the activation energy for the reaction of  $\text{BF}_3$  with amines is zero. Moreover, hydrogen-bonded complexes are formed rapidly [20] in solid solutions in nitrogen and argon at  $30^\circ\text{--}40^\circ\text{K}$ , so the exchange  $\text{HCl} + \text{DBr}$  is slow by comparison. Hence  $E_a > \delta$ , and so the assumption of [16] is not valid. Measurement of  $E_a$  by NMR [2] agrees with this result. It may well be that the exchange rate in  $\text{HCl} + \text{DBr}$  is governed by synchronous passage of the protons through the potential barrier separating the two minima on the potential-energy curve for the hydrogen bond.

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