distinguishes as "immanent" qualities, that characterize particular relationships, from "configurational" qualities, that are related to particular materials.

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RECOMBINATION OF CHLORINE ATOMS

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THE recombination of chlorine atoms has been the subject of two recent communications[1,2], Linnett and Booth[1] having obtained a value for the overall termolecular rate constant which is approximately two orders of magnitude less than that reported by Bader and Ogryzlo[2].

Both authors used the isothermal calorimetric technique[3] to measure the decay of the atom concentration. This method is known to give results of dubious reliability in the presence of excited species, and it is sometimes found that only a fraction of the energy of the atom recombination is accommodated on the catalytic wire[4]. We have used an alternative technique to monitor the atom concentration, and have therefore measured our rate constants by an independent method.

The atoms were produced in a flow system by a radio-frequency discharge through pure chlorine gas. The reaction cell was of 2·9 cm internal diameter and the walls were 'poisoned' with sulphuric acid[5].

Downstream from the point of injection of the chlorine atoms a multiperforated jet permitted the addition of nitrosyl chloride gas, which was used to estimate the absolute value of the atom concentrations by means of the fast reaction:

$$Cl + NOCl \rightarrow Cl_2 + NO$$

Chlorine was obtained from Imperial Chemical Industries, Ltd., and quoted as 99·99 per cent pure. The nitrosyl chloride was prepared by the reaction of nitric oxide with molecular chlorine and was purified by fractional vaporization. Pressures were measured on a McLeod gauge filled with sulphuric acid, which was standardized against a conventional mercury McLeod gauge.

For each experiment the absolute value of the chlorine atom concentration was determined at one position in the reaction tube by titration with nitrosyl chloride, and the relative concentrations of the atoms along the remainder of the tube were obtained by measurement of the intensity (I) of the red glow emitted from the recombining gas.

The dependence of I on the chlorine atom concentration was determined[6], and hence absolute values for its concentration obtained at several positions along the tube.

If the recombination mechanism is expressed[1,2]:

$$Cl + Cl + Cl_2 \xrightarrow{k_{Cl_2}} Cl_2 + Cl_2$$

$$Cl + \text{wall} \xrightarrow{k_w} \tfrac{1}{2}\, Cl_2$$

then

$$\frac{-d[Cl]}{dt} = 2\, k_{Cl_2}\,[Cl]^2\,[Cl_2] + k_w[Cl] \qquad (1)$$

From low-pressure experiments at low chlorine atom concentration a value for k_w of 0·70 sec^{-1} was obtained corresponding to a wall recombination efficiency (γ) = $3{\cdot}5 \times 10^{-5}$, which is in good agreement with previous work[2].

k_{Cl_2} was determined over a range of pressure and chlorine atom concentrations (Fig. 1); our results are approximately half those obtained by Bader and Ogryzlo, and k_{Cl_2} decreases with increase in chlorine atom concentration. Bader and Ogryzlo's results, which are plotted for comparison on the same graph, show the same general trend.

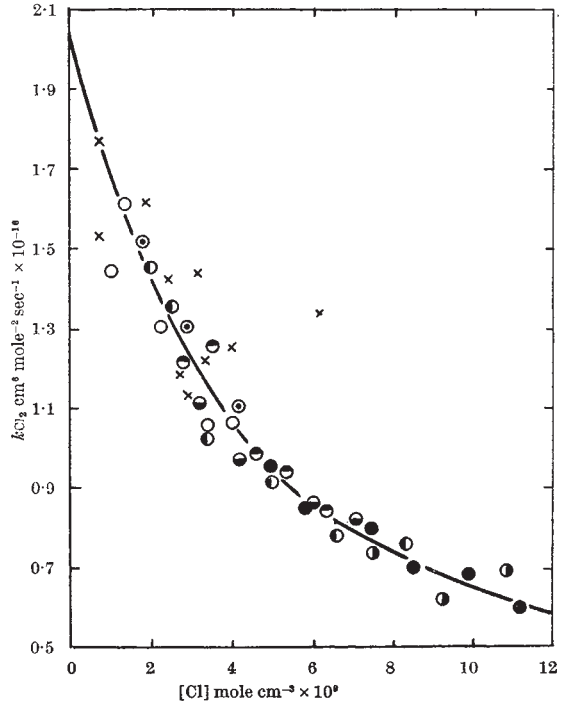

Fig. 1. Experimental values of k_{Cl_2} at the pressures (torr): ○, 2·03; ○, 1·65; ◐, 1·21; ◒, 0·91; ◓, 0·66; ◑, 0·58; ●, 0·33; ×, values obtained by Bader and Ogryzlo (divided by 2 for comparison)

Such a decrease is not in accordance with equation (1), which must therefore represent an over-simplified presentation of the reaction.

A more detailed mechanism for the removal of the chlorine atoms is:

$$Cl + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cl_3$$

$$Cl_3 + Cl \xrightarrow{k_2} Cl_2 + Cl_2$$

$$Cl + \text{wall} \xrightarrow{k_w} \tfrac{1}{2}\, Cl_2$$

Hence:

$$\frac{-d[Cl]}{dt} = \frac{2\, k_1\, k_2 [Cl]^2\,[Cl_2]}{k_{-1} + k_2[Cl]} + k_w[Cl] \qquad (2)$$

From equations (1) and (2) the measured overall termolecular rate constant (k_{Cl_2}) is given by:

$$k_{Cl_2} = \frac{k_1\, k_2}{k_{-1} + k_2\,[Cl]}$$

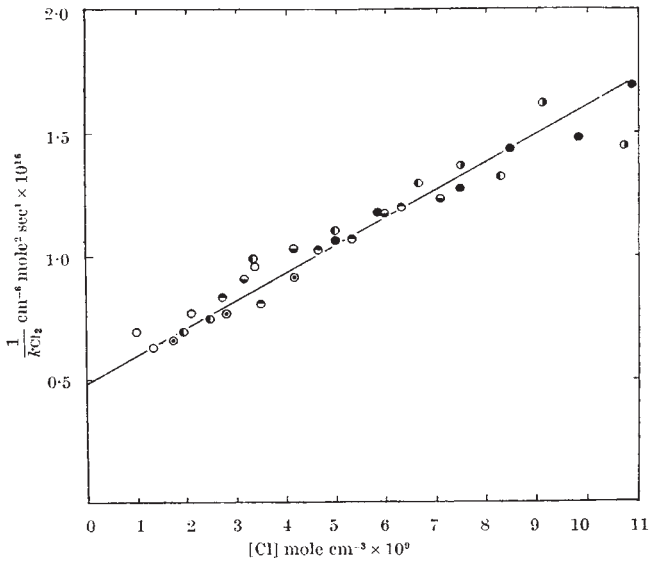

Fig. 2. Dependence of the reciprocal of the termolecular rate 'constant' on the atomic chlorine concentration

or:

$$\frac{1}{k_{Cl_2}} = \frac{[Cl]}{k_1} + \frac{k_{-1}}{k_1 k_2}$$

At very low concentrations where $k_{-1} \gg k_2$ [Cl], then $(k_{Cl_2})_{[Cl]\to 0} = \frac{k_1 k_2}{k_{-1}}$. $\frac{1}{k_{Cl_2}}$ is plotted against [Cl] in Fig. 2. The slope of the line gives $\frac{1}{k_1}$ and from the intercept we obtain $\frac{k_{-1}}{k_1 k_2}$.

From Fig. 2:

$$k_1 = 9{\cdot}09 \times 10^7 \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$$

and

$$\frac{k_1 k_2}{k_{-1}} = 2{\cdot}04 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$$

hence

$$\frac{k_2}{k_{-1}} = 2{\cdot}24 \times 10^8 \text{ cm}^3 \text{ mole}^{-1}$$

If we assume that the reaction of Cl and Cl_3 takes place with unit collisional efficiency, then we obtain an upper limit for k_2 of $1{\cdot}7 \times 10^{14}$ cm^3 mole^{-1} sec^{-1} and, by substitution, $k_{-1} \leqslant 7{\cdot}6 \times 10^5$ sec^{-1}.

At low atom concentrations:

$$\frac{[Cl_3]}{[Cl]} = \frac{k_1 [Cl_2]}{k_{-1}}$$

and at a pressure of 2 torr:

$$[Cl_3] \geqslant 1{\cdot}2 \times 10^{-5} [Cl]$$

The value of the termolecular rate constant obtained for chlorine atom recombination at very low atom concentrations ($2{\cdot}04 \times 10^{16}$ cm^6 mole^{-2} sec^{-1}) is in fairly good agreement with the value of 4×10^{16} cm^6 mole^{-2} sec^{-1} obtained by extrapolating Bader and Ogryzlo's data from experiments carried out in pure chlorine, and is in good agreement with their data from indirect determinations in the presence of inert gases.

A full account of this work is to be published in detail elsewhere. I thank Mr. H. Williams for helpful discussion and criticism.

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QUANTITATIVE DETERMINATION OF PROGESTERONE IN HUMAN PLASMA BY THIN-LAYER AND GAS-LIQUID RADIOCHROMATOGRAPHY

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In 1954, progesterone was isolated from human peripheral venous blood and the concentration determined in samples collected during late pregnancy[1]. Later, although several methods were developed for the determination of the hormone in plasma samples of reasonable volume[2-4], it was apparent that a considerable increase in sensitivity would be required for the determination of plasma concentrations in early pregnancy and the menstrual cycle. For this purpose and to achieve a higher degree of specificity, the method developed in this department[2,4] which involved alumina chromatography and the formation of the isonicotinic acid hydrazone, was modified by the introduction of preliminary purification on silica gel, followed by paper chromatography and the formation of the thiosemicarbazone. There was a ten-fold increase in sensitivity and, using an internal standard of progesterone-4-^{14}C, the method was suitable for the assay of 10-ml. samples collected during the luteal phase of the menstrual cycle[5]. Further information on the plasma concentration of the hormone during the cycle has been obtained by a double isotope dilution technique[6] and the application of a fluorimetric method has been reported[7]. However, the former technique is time-consuming and expensive, while the latter is liable to interference by non-specific material.

In general, physicochemical methods for the determination of steroids in blood are inconveniently laborious—specificity being achieved by the use of several chromatographic steps and re-chromatography of a derivative. The time involved in the analysis may be from 3 to 14 days. The introduction of gas-liquid chromatography for steroid analysis offered the hope of a more rapid and, at the same time, highly sensitive and specific method. There were, however, two main problems—to effect adequate preliminary separation without resort to laborious techniques and to ensure that the method is quantitative. The present report describes the manner in which the former has been resolved by the use of two-dimensional thin-layer chromatography; the latter by the simultaneous determination of an isotopically labelled internal standard in terms of integrated radioactivity. The new method has a high degree of specificity and the sensitivity is adequate for the determination of the hormone in 5-ml. samples of pregnancy plasma and 10-ml. samples collected during the menstrual cycle. The time involved is three hours plus the duration of the gas-liquid radiochromatography (40–80 min depending on choice of temperature and stationary phase).

While this work was in progress there were preliminary reports on the application of gas-liquid chromato-