ISOTPOIC EXCHANGE REACTIONS

KINETICS OF ISOTOPIC EXCHANGE REACTIONS PART 6.—THE THERMAL CARBON MONOXIDE + PHOSGENE SYSTEM

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Received 28th June, 1954; in final form, 30th September, 1954

The rates of the thermal exchange between 14 C-labelled carbon monoxide and phosgene, in the presence of an equilibrium pressure of chlorine, have been measured from 375° to 450° C. An exchange mechanism has been postulated which is consistent with earlier non-tracer thermal studies on phosgene. From the corresponding rate law, the observed exchange rates may be adequately reproduced by assuming values for a composite rate constant close to those reported by Bodenstein and Plaut.

An investigation of the thermal exchange,

 $^{14}CO + COCl_2 \rightleftharpoons CO + ^{14}COCl_2$,

has been performed to supplement work reported ¹ on the photochemical exchange system. Previous workers ², ³ have shown that in the region of $350^{\circ}-450^{\circ}$ C the rates of phosgene formation and decomposition are measurable and may be explained by the reaction scheme :

$$M + Cl_2 \rightleftharpoons Cl + Cl + M \quad K_{Cl}$$

$$CO + Cl \rightleftharpoons COCl \quad K_{COCl}$$

together with, for formation,

 $\text{COCl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl} \qquad k_4$

or for decomposition,

$$\text{COCl}_2 + \text{Cl} \rightarrow \text{COCl} + \text{Cl}_2 = k_1$$

An alternative scheme, involving the Cl_3 intermediate rather than COCl, is possible but the above scheme is usually favoured.⁴ Bodenstein and Plaut ² have shown that the rate of phosgene formation is given by

 $\log k_F = \log \left\{ k_4 K_{\rm Cl}^{\frac{1}{2}} / K_{\rm COCl} \right\} = - (5741/T) + 8.023,$

and the rate of decomposition by

$$\log k_D = \log\{k_1 K_{C1}^{\ddagger}\} = -(11451/T) + 13.483.$$

However, Christiansen 3 has represented the latter rate as

 $\log k_D = -(11420/T) + 15.154.$

It was considered that a choice between these two divergent rate constant values might be possible from an evaluation of the rates of the isotopic exchange.

EXPERIMENTAL

The purification and isotopic assay of the gases have been described in the previous report.¹ Sampling of the exchanging gas mixture at constant pressure required the gas to be heated in separate, identical reaction vessels and the total contents of individual vessels to be assayed at known times. A typical reaction vessel consisted of a Pyrex

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tube (8 mm int. diam., 150 mm length) to which was sealed 2 mm capillary tubing (80 mm length), a vacuum stopcock and a B 7 cone. Such tubes were inserted reproducibly into an electric furnace such that the unheated (capillary) portion constituted only 0.1 % of the gas volume. Aluminium radiation shields permitted the use of Apiezon grease T on stopcocks without introducing leakage difficulties. The temperature of the furnace, as measured by a calibrated chromel-alumel couple, was maintained to $\pm 0.1^{\circ}$ C by d.c. heating; temperature variation between different reaction tubes within the furnace, and along the length of an individual tube, was about $\pm 0.06^{\circ}$ C.

To prevent thermal decomposition of the phosgene ⁵ at the high temperatures used in this study, chlorine was added to the ${}^{14}CO + COCl_2$ gas mixture at a pressure corresponding to the dissociative equilibrium pressure of phosgene at the reaction temperature. The K_p values of Bodenstein and Plaut ² were used.

In a typical exchange run, six reaction vessels were filled with the requisite pressures of ¹⁴CO, COCl₂ and Cl₂ and thermally equilibrated in an auxiliary furnace at 370° C, before insertion in the main furnace at the reaction temperature. Five minutes were sufficient for final thermal equilibration. After this time the first tube was withdrawn and plunged into liquid air to separate the condensable gases from the CO; this represented the zero-time sample. The activity of the phosgene and carbon monoxide fractions was then determined with the ionization chamber and G.-M. counter respectively, as described in the previous paper. (Because of exchange in the thermal equilibration period, the phosgene fraction contained some activity, whilst the carbon monoxide fraction had correspondingly lost some activity. These activity values were taken as A_0 in the calculation of the fraction of exchange γ , where $\gamma = (A_0 - A_t)/(A_0 - A_\infty)$; because of the first-order rate characteristics of the exchange, no error is thereby introduced.⁶) Thereafter four other samples were withdrawn and sampled at known times. A sixth sample served to provide the A_{∞} value. The exchange half-times, determined by the two assay procedures, were identical and the reproducibility of the composite $t_{\frac{1}{2}}$ value was normally ± 3 %. A graphical plot of log $(1 - \gamma)$ against t has not been given because of the close resemblance to that for the photochemical runs.

RESULTS

ISOTOPE EFFECT FACTOR

The mean value of the exchange equilibrium constant ϵ as measured by two independent assay techniques, has been reported ⁷ as 1.0124 (400° C), 1.0055 (450° C) and 1.0020 (500° C). Values at intermediate temperatures were obtained by interpolation. In all cases experimental values of A_{∞} agreed quite well with values calculated from reactant pressures and the isotope effect factor.

REACTION CONDITIONS

A large increase in available surface within the reaction vessel, effected by the introduction of both granulated and fibrous Pyrex glass, caused no measurable alteration in exchange rate. The introduction of oxygen up to partial pressures of 20 mm Hg caused no marked decrease in the exchange rate. All exchanges were performed in the dark as the exchange is still photosensitive in the long u.-v. region.

VARIATION OF REACTANT PRESSURES AND TEMPERATURE

Since the partial pressures of phosgene, carbon monoxide and chlorine are interrelated by an equilibrium constant, it was not possible to measure exchange rates as a function of a single gas pressure whilst the other two were held constant. Therefore sets of experiments were conducted in which one gas pressure was held constant whilst the other two were varied. Most exchanges were conducted at 400° C, at which temperature half-times varied between 50 and 360 min. Measurement of exchange rates at 420° and 450° was more difficult since half-times fell to 10 min or less. At 500° exchange was complete in 5 min, the time required to equilibrate thermally the reactants. The observed reciprocal exchange half-times are recorded in table 1.

DISCUSSION

The insensitivity of the exchange rate to introduced oxygen of various pressures is as observed in non-tracer studies and indicates a similarity in reaction mechanism. In the region of 400° negligible oxidation by contaminating oxygen of CO + Cl_2

mixtures occurs compared to the rate of phosgene formation.² Hence the most probable exchange mechanism may be written thus :

$$M + Cl_2 \rightleftharpoons Cl + Cl + M \qquad K_{Cl} = [Cl]^2 / [Cl_2]$$

$$COCl_2 + Cl \rightarrow COCl + Cl_2 \qquad k_1$$
(1)

$$COCl \rightleftharpoons CO + Cl \qquad K = [CO][Cl]/[COCl] \qquad (2)$$

$$^{14}CO + Cl \rightleftharpoons ^{14}COCl$$
 $K' = [^{14}CO][Cl]/[^{14}COCl]$ (2')

Using the relation $K_p = [CO][Cl_2]/[COCl_2] = k_1K/k_4$, making the customary assumptions that equilibria (2), (2') and (3) are continuously maintained and employing steady-state approximations, the rate law corresponding to the postulated exchange mechanism may be written :

$$0.693/t_{\pm} = (k_1 K_{C1}^{\frac{1}{2}} \epsilon' a c_{\pm}/b) + k_1' K_{C1}^{\frac{1}{2}} c_{\pm}^{\frac{1}{2}},$$

where a = phosgene pressure, b = carbon monoxide pressure, c = chlorine pressure,

$$\epsilon' = \frac{k_4' K}{k_4 K'} = \frac{[{}^{14}\text{COCl}_2]}{[\text{COCl}_2]} / \frac{[{}^{14}\text{CO}]}{[\text{CO}]} = \epsilon.$$

The entity M may be identified as either a gaseous molecule or as "wall"; hence the rate law shows that exchange half-times ought to be independent of the area and nature of the available surface, as is observed.

TABLE 1.—VARIATION OF EXCHANGE RATE WITH REACTANT PRESSURES AND TEMPERATURE

run	temp.	[COCl ₂]	[CO]	[Cl ₂]	1/t1	cal	calc. $1/t_{\frac{1}{2}}$	
no.	°C	cm Hg	cm Hg	cm Hg	$\times 10^{-3} \text{ min}^{-1}$	I	п	
14	375.0	4.20	2.62	12.82	1.14	1.14	1.24	
24	400.0	0.87	1.31	11.55	2.78	2.76	3.39	
25	400.0	1.74	1.31	23.14	5.61	5.49	6.75	
26	400·0	2.63	1.31	34.66	8.82	8.66	10.63	
30	400.0	3.48	1.31	46.20	11.9	12.2	15.0	
31	400.0	4.36	1.31	57.80	15.9	16.2	19.9	
32	400.0	5.23	1.31	69.37	20.2	20.4	25.1	
27	400.0	3.48	0.87	69.37	20.6	20.4	25.2	
28	400.0	3.48	1.31	46.20	12.5	12.2	15.0	
29	400.0	3.48	1.74	34.66	8.62	8.66	10.6	
18	400.0	3.48	2.63	23.12	5.52	5.47	6.73	
19	400.0	3.48	3.48	17.34	4.02	4.08	5.01	
20	400.0	1.53	0.44	60.96	17.1	17.2	21.2	
21	400.0	3.06	0.87	60.96	17.2	17.3	21.3	
22	400.0	4.59	1.31	60.96	17.5	17.2	21.2	
23	400.0	6.13	1.74	60.96	17.3	17.4	21.4	
33	400.0	7.66	2.18	60.96	17.3	17.3	21-3	
34	400.0	9.19	2.63	60.96	17.3	17.3	21.3	
15	420.0	1.00	1.31	24.00	13.0	13.0	16.0	
16	420.0	1.74	1.31	49-24	25.0	24.6	30.4	
17	420.0	3.48	3.48	31.44	16.7	16.9	20.8	
35	450 ∙0	0.87	1.31	46.00	78.1	80.9	100.0	
36	450·0	1.00	1.31	52.75	94.4	91.7	113.7	
37	500.0	0.80	4.00	63.60	" inst "	1227	1510	
38	500·0	1.60	8.00	63.60	" inst "	1227	1510	

calc. I, $\log\{k_1 K_{CI}^{\frac{1}{2}}\} = -(11440/T) + 13.38$,

calc. II, $\log\{k_1 K_{Cl}^{\frac{1}{2}}\} = -(11451/T) + 13.48$.

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It is not possible to subject the exchange data to graphical plots since the three gas pressures are not independent variables. However, it is seen from the rate law, that at constant a/b (and hence c) the exchange half-times ought to be constant. This is seen to be the case within the experimental error of ± 3 %, in the series of runs: 20, 21, 23, 33, 34, and for the pairs of runs: 18, 25; 26, 29; 28, 30; and 27, 32. A further test of the exchange data with the deduced rate law is the comparison of observed exchange rates with those calculated from values of the effective rate constant $k_D = k_1 K_{Cl}^{\frac{1}{2}}$, already evaluated by Bodenstein and Plaut, and Christiansen. From the kinetics of the postulated exchange mechanism, the observed isotope effect does not arise in the rate constants k_1 and k_1' ; thus k_D can also be set equal to $k_1' K_{Cl}^{\frac{1}{2}}$. Converting the Bodenstein values to the appropriate units, the calculated reciprocal half-times have been listed in table 1 as calc. II Although these values are of the correct order of magnitude, they are consistently higher than the observed values. Moreover, the rate values reported by Christiansen give $1/t_1$ values which are roughly fifty times greater than the observed (e.g. for the conditions of run 14, table 1, $1/t_1$ (calc.) = 57.1 × 10⁻³ min⁻¹, whereas $1/t_{\frac{1}{2}}$ (obs.) = 1.14); half-times calculated from this source have therefore been omitted from table 1. Best correspondence between calculated (calc. I) and observed rates is obtained using the rate values,

$$\log k_D = -(11440/T) + 13.38.$$

In this case, between 375° and 450° C, positive and negative differences between observed and calculated values occur to an equal extent. All such differences are 3 % or less, which is the magnitude of the experimental uncertainties in the half-times. The extreme rapidity of exchange above 450° C, precludes any further comparison of values. The composite activation energy term in the above equation is very close to those reported by both Bodenstein and Plaut, and Christiansen, whereas the frequency term agrees well with that reported by the former workers. These facts indicate that the observed exchange rates are described quite adequately by the deduced rate law. Conversely these conclusions lend support to the preference, already expressed,⁴ for the results of Bodenstein and Plaut.

Finally it ought to be noted that the exchange isotope effect is expressed in terms of the reactions :

$${}^{12}\text{COCl} + \text{Cl}_2 \rightarrow {}^{12}\text{COCl}_2 + \text{Cl}$$
$${}^{14}\text{COCl} + \text{Cl}_2 \rightarrow {}^{14}\text{COCl}_2 + \text{Cl}$$

and the equilibria:

 ${}^{12}\text{COCl} \rightleftharpoons {}^{12}\text{CO} + \text{Cl}$ ${}^{14}\text{COCl} \rightleftharpoons {}^{14}\text{CO} + \text{Cl}$

in both the postulated thermal and photochemical exchange mechanisms. These two mechanisms, based upon reactions of the COCl radical, are therefore mutually consistent.

The award of an I.C.I.A.N.Z. Research Fellowship to the author by the University of Melbourne is acknowledged.

¹ Stranks, Trans. Faraday Soc., 1955, 51, 514.

² Bodenstein and Plaut, Z. physik. Chem., 1924, 110, 399.

- ³ Christiansen, Z. physik. Chem., 1923, 103, 99.
- ⁴ Schumacher, Chemische Gasreactionen (Steinkopff, 1938), p. 444.
- ⁵ Bodenstein and Dunant, Z. physik. Chem., 1908, 61, 437.
- ⁶ Norris, J. Physic. Chem., 1950, 54, 777.

⁷ Stranks, Trans. Faraday Soc., 1955, 51, 499.