

CHROM. 4897

A SECOND-ORDER REACTION ON A GAS CHROMATOGRAPHIC COLUMN

II. DECOMPOSITION OF IBr ON A CHROMATOGRAPHIC COLUMN

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SUMMARY

The computational analysis described in Part I¹ is applied to the behaviour of the system Br₂-IBr-I₂ on a column of Kel-F grease supported on teflon powder. The experimental results are well matched by computations for instantaneous reaction. This implies a rate constant $k \gtrsim 5 \times 10^4 \text{ l mole}^{-1}\text{sec}^{-1}$ and an activation energy $E_a \lesssim 10.6 \text{ kcal mole}^{-1}$ for the decomposition of IBr in solution in Kel-F grease at 94°.

EXPERIMENTAL

The apparatus is essentially a gas chromatograph in which the whole flow system is made of pyrex glass, except that the detector block is stainless steel (SS 316). The detector is a thermal conductivity cell with teflon-clad tungsten filaments (from Gow Mac). The attenuator of an Aerograph AgO P3 chromatograph was used.

Column

The column consisted of 4.5 m × 5 mm I.D. pyrex tubing, containing 10% Kel-F grease No. 90 (chlorofluorocarbon) coated on Chromosorb T (teflon powder). The coating was done by dissolving the Kel-F grease in chloroform, mixing with the Chromosorb T, and drying over a water bath. Since the dry product is difficult to pack evenly in the column (probably because it easily acquires electrostatic charge), the coated Chromosorb was made into a slurry with a mixture of equal volumes of acetone and water, which does not dissolve the coating. The slurry was introduced into pyrex tubing, previously bent into shape for fitting into the oven of the gas chromatograph, with a glass wool plug at the end of the tubing, and with suction applied by means of an aspirator.

Standard operating conditions

The operating conditions were as follows: Filament current: 200 mA; flow rate: 76.0 ml/min at the exit (room temperature, atmospheric pressure); temperatures: injector 180°, column 93–95° and detector 130°; inlet pressure: 1.5 atm.

Calibration

Solutions of bromine and iodine (both Baker Analyzed Reagent Grade) in ethylene dibromide (B.D.H. Reagent Grade) were injected quantitatively by means of Hamilton microsyringes, and the peak areas were measured by a disc integrator attached to the recorder (Leeds and Northrup Speedomax H). Both lay on the same linear calibration curve of peak area *versus* moles injected. Mixtures of Br_2 and I_2 were injected quantitatively; this time three overlapping peaks appeared on the chromatogram (Fig. 1). The first and third peaks corresponded to Br_2 and I_2 , re-

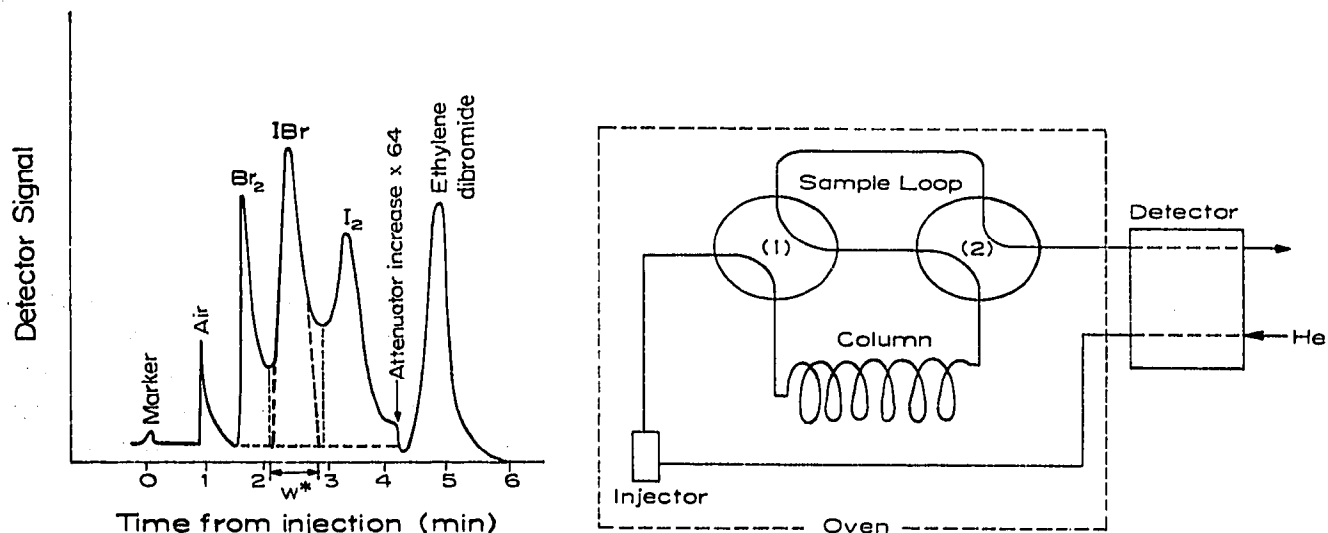


Fig. 1. A typical chromatogram.

Fig. 2. Apparatus for recycling experiment. 1 and 2 are four-way stopcocks.

spectively, and the centre one was assigned to IBr . The total area of the three peaks, plotted against total moles of Br_2 and I_2 injected, fell on the same straight line as the separate Br_2 and I_2 calibrations. Therefore the calibration curve for IBr was taken to be that same straight line.

Procedures

Solutions of equimolar amounts of bromine and iodine in ethylene dibromide were injected quantitatively. All operating conditions were maintained at the standard values given above except where one of them was being varied to test its effect. The ranges of those variations were: volume injected, 1–10 μl ; flow rate, 20.7–122.0 ml/min; injector temperature, 150–189°; column temperature, 88–100°. The standard solution for injection contained 0.19 mole/l of total Br_2 and I_2 , and solutions from 0.096–0.503 mole/l were used to test the effect of concentration.

To demonstrate unequivocally that reaction was occurring on the column, the apparatus in Fig. 2 was used to recycle a part of the eluted material through the column. 10 μl of a solution was injected. The appearance of the signal was observed on the recorder, and the middle part of a peak was trapped in the sample loop by turning stopcock (2) through 90° at the appropriate moment. In separate runs, each of the three peaks of the elution profile was sampled in this way. After the elution

was over, the sample trapped in the loop was fed into the gas chromatograph again by turning stopcock (1) through 90°. The volume of the sample loop was 5.7 ml, and that of each peak was about 60 ml.

The characteristics of the chromatograms were expressed numerically by calculating the parameters K_{eff}^* and W^* , as defined in Part I: K_{eff}^* is the area of the centre part of the chromatogram divided by the product of the areas of the first and third parts, the lines of division being taken at the minima in the profile; W^* is the distance in volume units between the intersections with the horizontal axis of tangents at the inflection points of the centre peak. A typical chromatogram is shown in Fig. 1.

RESULTS AND DISCUSSION

Calibrations

The retention volume of air, V_{RAIR} , was used as an approximation to V_{RI} , the retention volume of a component insoluble in the stationary phase, and was $V_{RAIR} = 82.3$ ml. Retention volumes of the three components of the reaction mixture were: Br_2 , 135.0 ml; IBr , 199.0 ml; I_2 , 270.0 ml.

The number of theoretical plates calculated from the retention volume and bandwidth of the I_2 peak was $n = 500 \pm 80$.

Recycling experiment

Fig. 3 shows the results of recycling a cut from each peak in the eluted material.

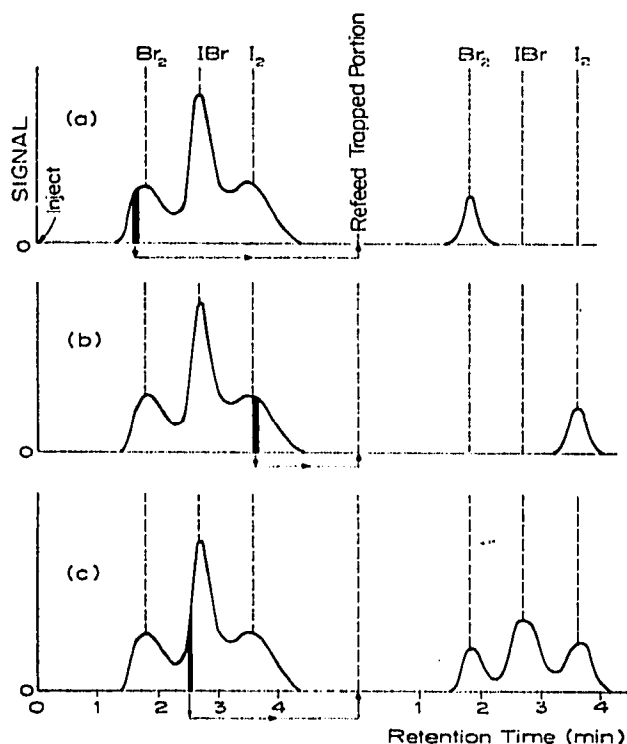


Fig. 3. Results of a recycling experiment. The shaded bands are the trapped portions of eluted material. Peak heights not to scale; attenuation is reduced by a factor usually of 10–20 between original chromatogram and recycled sample. In (c) $K_{\text{eff}}^* = 5.0$ and 1.5 in original and recycled material, respectively.

TABLE I

DATA SHOWING THAT CHANGES IN SOME CONDITIONS DO NOT AFFECT K_{eff}^*

	<i>Time from preparation of solution to injection (h)</i>							
	2.0	2.5	3.0	23				
K_{eff}^*	4.5	4.5	4.7	4.6				
	<i>Injector temperature (°C)</i>							
	150	160	172	189				
K_{eff}^*	5.5	5.2	4.7	6.0				
	<i>Flow rate (ml/min)</i>							
	20.7	28.5	37.4	40.0	53.9	76.0	96.7	122.0
K_{eff}^*	4.2	3.8	4.4	4.6	4.0	4.5	4.3	5.2

The sample from the first peak gave only a bromine peak on recycling, and the sample from the third peak gave only an iodine peak. The sample from the centre peak, however, gave on recycling three peaks again, with a value of K_{eff}^* even smaller than that of the original chromatogram (1.5 in place of 5). This is conclusive evidence that reaction is occurring in the column. It indicates also that K_{eff}^* depends on the total amount of sample, as is expected from the $K_{\text{eff}}^* - V_0$ behaviour predicted by computation (Part I, Fig. 3). Study of the dependence of K_{eff}^* on a number of variables, as described below, in fact showed that the total amount of the sample was the most important variable.

Dependence of K_{eff}^ on various conditions*

Limits of error in calculating K_{eff}^* from chromatograms are fairly large, because of the difficulty of locating precisely the minima between the peaks, and are estimated at $\pm 15\%$. Limits of error on W^* are $\pm 10\%$. Within these limits, K_{eff}^* was found to be independent of the following:

- time from preparation of solution to injection, which might affect the amount of IBr formed in the solution before injection (Table I);
- injector temperature (Table I);
- concentration of the sample (Fig. 4a);
- flow rate (Table I).

The last-mentioned observation is an important one, since it is expected only for $k_0 = \infty$, and therefore suggests very rapid reaction. Further evidence for a high k_0 is provided by the strong dependence of K_{eff}^* on the total amount of sample (Fig. 4a), in which K_{eff}^* exhibits some very low values, but varies monotonically with amount of sample, showing no minimum. It is not quite clear what variable is best to use in displaying this variation. As mentioned in Part I, the feed pulse volume, which is the convenient variable for computations, is not accessible to direct experimental measurement. It can be calculated from W^* on the assumption that $k_0 = \infty$, but there is a large uncertainty in the lowest V_0 values, since V_0 varies very rapidly with W^* in

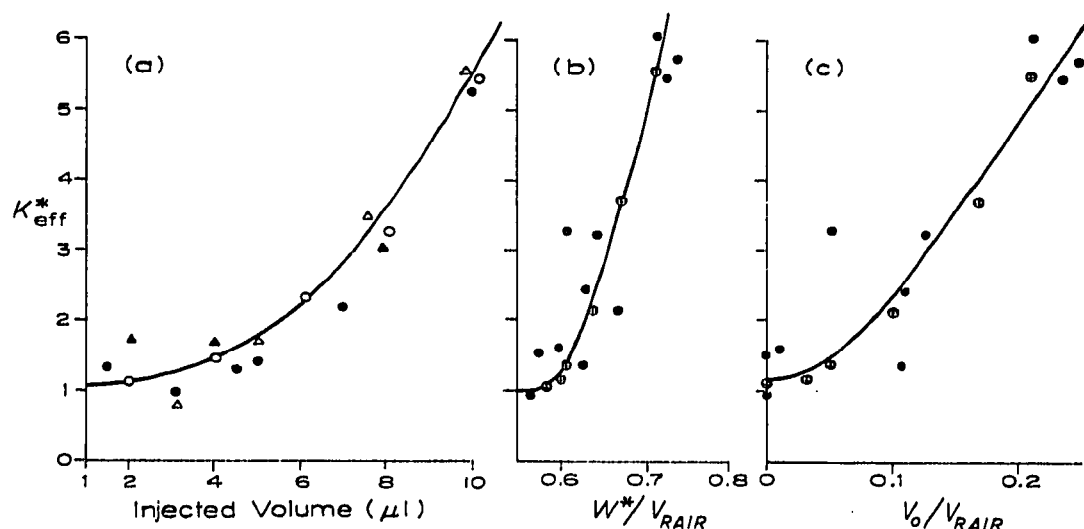


Fig. 4. Apparent equilibrium constant K_{eff}^* plotted against (a) injected volume, (b) centre band width W^* , and (c) feed pulse volume calculated from W^* assuming instantaneous reaction. In (a), symbols specify total concentration in injected solution: \blacktriangle , 0.0963 mole/l; \circ , 0.1375 mole/l; \bullet , 0.1925 mole/l; \triangle , 0.503 mole/l. In (b) and (c), solid circles are experimental points and open circles are computed points for instantaneous reaction.

this region. Three variables are used in Figs. 4a, b and c: the total amount injected; the centre bandwidth W^* ; and V_0 calculated from W^* . Figs. 4b and c also show some computed values of K_{eff}^* , for $k_0 = \infty$, for comparison with the experimental ones. These computations and the computation of V_0 from W^* were carried out in the same manner as the computations in Part I, but with the new values $n = 500$ and $K_e = 169$ (at 95°). The latter value is calculated from standard thermochemical data^{2,3} for the reaction $\text{I}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{IBr}(\text{g})$, which yield $\Delta G^\circ = -2720 - 2.80 T$ cal/mole. The composition of the feed pulse had little effect on the computed value of K_{eff}^* , and was taken as the equilibrium composition in most computations (for example, at $V_0/V_{\text{RAIR}} = 0.0983$, the equilibrium composition $A_0 = C_0 = 1.00$, $B_0 = 14.75$ and the very much out-of-equilibrium composition $A_0 = B_0 = C_0 = 5.00$ yield, respectively, 2.09 and 1.95 for K_{eff}^*).

Computations for the value $k_0 = 200$, the highest finite value used, are close to the limit of reliability of the computer programme at computation times we could afford (some runs took 40 min). The total amount of material in the computed elution curve sometimes differed by as much as a few percent from the amount specified in the input pulse, and computed K_{eff}^* and W^* should be considered to have error limits of $\pm 5\%$. In this connection it should be recognized that the plate theory was used in computations (as described in Part I) because a more sophisticated programme to solve differential equations allowing explicitly for diffusion, etc., was found incapable of handling high reaction rates in a reasonable time. The programme used for instantaneous reaction (see Part I) was both faster and much more reliable, as indicated by the match of total input to total output, than that for finite rates at its practical limit of $k_0 = 200 \text{ ml min}^{-1} (\text{conc. unit})^{-1}$.

The lower limit of the rate constant k

Figs. 4b and c show good agreement between observed values and those computed

for $k_0 = \infty$. The family of curves in Fig. 3 of Part I indicates that conspicuous changes in the curve from its $k_0 = \infty$ form occur only below $k_0 = 100$, and the indication of high reaction rate is thus, more precisely, $k_0 > 100 \text{ ml min}^{-1} (\text{conc. unit})^{-1}$. The arbitrary concentration unit is to be found, in any comparison with experiment, by equating the total input pulse concentration in the computation to that in the experiment. For all computed points in Figs. 4b and c, concentrations were $A_0 = C_0 = 1$, $B_0 = 14.75$, total 16.75 concentration units. If the experimental concentration is α mole/l, then the inequality becomes $k_0 > (1675/\alpha) \text{ ml min}^{-1} (\text{mole/l})^{-1}$. Clearly, the lower the value of α to which we find agreement between experiment and the "high k_0 " computed curves, the more restrictive this condition becomes. In the present experiments, the lowest α arises from an injected solution of $10 \mu\text{l}$ with a total I_2 and Br_2

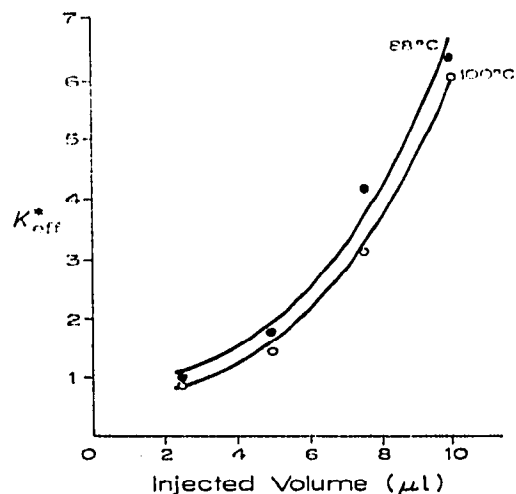
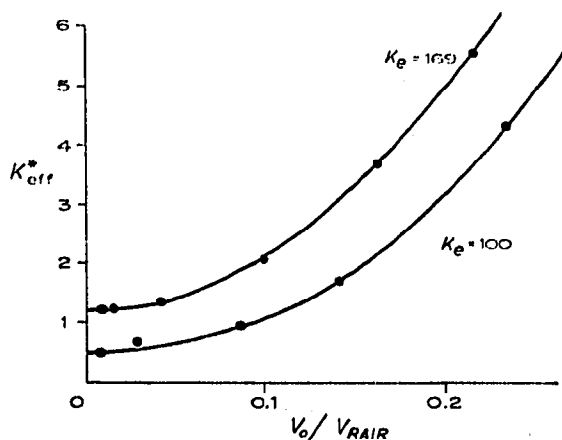


Fig. 5. K_{eff}^* against feed pulse volume V_0 for two values of the true equilibrium constant K_e . $n = 500$, $w = 76 \text{ ml/min}$, $k_0 = \infty$ (computed points).

Fig. 6. K_{eff}^* against injected volume for two column temperatures; experimental results.

concentration in solution of 0.0963 mole/l. To convert this into a gas phase concentration a after evaporation of the injected solution, the pulse volume V_0 is found from Figs. 4a and 5, which yield, for $10 \mu\text{l}$ solution, $V_0 = 0.21 V_{\text{RAIR}} = 0.21 \times 82.3 \text{ ml} = 17.3 \text{ ml}$. Hence $a = 0.0963 \text{ mole l}^{-1} \times 10^{-5} \text{ l}/17.3 \text{ ml} = 5.5 \times 10^{-5} \text{ mole l}^{-1}$. Hence the inequality becomes $k_0 \geq 3.0 \times 10^7 \text{ ml min}^{-1} (\text{mole/l})^{-1}$.

k_0 may be converted into the rate constant k by $k = k_0/K_B^2 V_L$, where $V_L = (V_{\text{RB}} - nV_G)/K_B = (V_{\text{RB}} - V_{\text{RAIR}})/nK_B = (199.0 - 82.3)/nK_B = 116.7/nK_B$. Since nV_L is the total volume of the Kel-F grease coating, which can be calculated from its known weight of 7 g and density of 2.4 g/ml as 3 ml, $K_B = 116.7/nV_L = 116.7/3 = 39$.

Then $k \geq 3.0 \times 10^7 / [(39)^2 \times (3/500)] \text{ l min}^{-1} \text{ mole}^{-1} = 5 \times 10^4 \text{ l sec}^{-1} \text{ mole}^{-1}$.

A very similar estimate can be made from the absence of flow rate dependence of K_{eff}^* . An examination of the behaviour of various parameters in the computations showed that, to a good approximation, a β -fold increase of flow rate should have the same effect on K_{eff}^* as a β -fold decrease in k_0 . We examined the effect of a 6-fold increase in flow rate, and found no change in K_{eff}^* (Table I). Since K_{eff}^* becomes fairly strongly dependent on k_0 below $k_0 = 50$, this indicates $k_0 \geq 6 \times 50 = 300$.

This is three times the previous estimate, but the flow rate experiments were at twice the concentration of the previous calculation, so that the two estimates of the lower limit of k are only a factor of $3/2$ apart.

Since second-order rate constants for reactions in liquid solutions are commonly of the order $k \sim 10^{11} \exp(-E_A/RT) \text{ l sec}^{-1}\text{mole}^{-1}$, the lower limit given here corresponds to $E_A \lesssim 10.6 \text{ kcal/mole}$ for the decomposition of IBr in solution in Kel-F grease.

The effect of column temperature

Fig. 6 shows that K_{eff}^* values at 100° lay consistently below those for 88° column temperature. The ratios for the four pairs of points in Fig. 6 are $K_{\text{eff}}^*(100^\circ)/K_{\text{eff}}^*(88^\circ) = 0.85, 0.80, 0.75, 0.95$, mean 0.84 ± 0.04 . The stated limit of error is better than that which would be expected from the $\pm 15\%$ limits given above for individual K_{eff}^* values, which would indicate 0.84 as only just significantly different from unity in an average of four pairs of readings.

Computations showed (Fig. 5) that although the numerical values of K_{eff}^* are very different from the true equilibrium constant K_e , changes in K_e are nevertheless reflected in roughly proportionate changes in K_{eff}^* . The two values of K_e used in the computations of Fig. 5 are in the ratio $100/169 = 0.59$. The ratio of K_{eff}^* values varies from 0.40 at $V_0/V_{\text{RAIR}} = 0$ to 0.60 at $V_0/V_{\text{RAIR}} = 0.2$. For the two temperatures used in the experimental work, K_e values from the usual thermochemical data yield $K_e(100^\circ)/K_e(88^\circ) = 160.5/181.3 = 0.885$, to be compared with the K_{eff}^* ratio of 0.84 .

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