217. *The Kinetics of the Decomposition of Carbonyl Selenide on an Allotropic Selenium Surface.*

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FEW heterogeneous gas reactions are known in which the catalytic surface is continuously renewed by the deposition of one of the reaction products from the gas phase. This is unfortunate, since such a process should be a good one for maintaining a constant catalytic surface, and for showing any change of the surface with temperature or other reaction conditions. Stibine, which decomposes at room temperatures, was studied by Stock and Bodenstein (*Ber.*, 1907, **40**, 570), who found that, after a sufficiently thick initial coating of antimony had deposited on the reaction bulb, reproducible values were obtained which could be expressed by $dp/dt = kp^n$. This was shown to be due to the change with pressure p of the amount of stibine adsorbed on the surface. The splitting up of carbonyl selenide into carbon monoxide and selenium appeared to provide another example of this type of reaction. The substance was first prepared in a state of purity by Pearson and Robinson (J., 1932, 652), who described it as a colourless liquid, b. p. — 22·9°/725 mm., m. p. — 122·1°, readily decomposed by heat. They found that, when perfectly dry, it could be kept at room temperature for considerable periods without change. The simplicity of the reaction and the absence of side reactions suggested that the kinetics of the decomposition would be worthy of study. This has proved to be the case, for it has been found that the selenium surface on which the reaction proceeds can exhibit phase allotropy. Its catalytic activity changes with the allotropic transformations, but a means has been found of accounting for the complications thereby introduced.

EXPERIMENTAL.

(a) *Preparation and Re-determination of Vapour Pressure of Carbonyl Selenide.*—The carbonyl selenide was prepared by Pearson and Robinson's method (*loc. cit.*) by passing pure dry carbon monoxide over molten selenium at a dull red heat and condensing the product in liquid oxygen. We used silica instead of porcelain reaction tubes, and the yield was thus increased four-fold while the carbon dioxide present was much reduced. This is probably due to the well-known catalytic activity of porcelain for the reaction $2CO \longrightarrow CO_2 + C$; the porcelain might also have been slightly porous and have allowed some atmospheric oxygen to come into the reaction tube, there combining with the carbon monoxide.

The carbonyl selenide was purified after being transferred to a storage apparatus shown in Fig. 1. Small head fractions were then distilled from the liquid when near its m. p. until the vapour pressure of the residue, in a bath of solid carbon dioxide and ether, was constant. It was apparent after the first preparation that Pearson and Robinson's vapour-pressure results were considerably high, and consequently a new series of determinations was made.

A middle fraction of the already purified carbonyl selenide was transferred to a condensation tube, and the pressure of the vapour above the liquid read on a mercury manometer to 0·05 mm. with the aid of a cathetometer. Constant-temperature baths were prepared from the purest obtainable organic liquids, which were partly frozen with liquid nitrogen, and the well-stirred mixture was then placed around the tube containing the carbonyl selenide. The temperatures of the baths were checked by readings on a thermocouple. The results are shown in Table I, P being the vapour pressure (in cm. Hg) and T the absolute temperature. When log P was plotted against $1/T$ a straight line was obtained, and the b. p. found by extrapolation to be — 22·8°/725 mm. This agrees well with the value of — 22·9° obtained by Pearson and Robinson when they made a separate determination of the b. p. by a dynamic method at the above pressure. There can be little doubt that the previous high values were due to the presence of carbon dioxide, as large amounts of this material were found by Pearson and Robinson in their crude preparation. From the slope of the line of the log P–$1/T$ curve the latent heat of vaporisation was calculated to be 49·3 cals. per g., a value that agrees well with that anticipated from Trouton's rule.

Fig. 1.

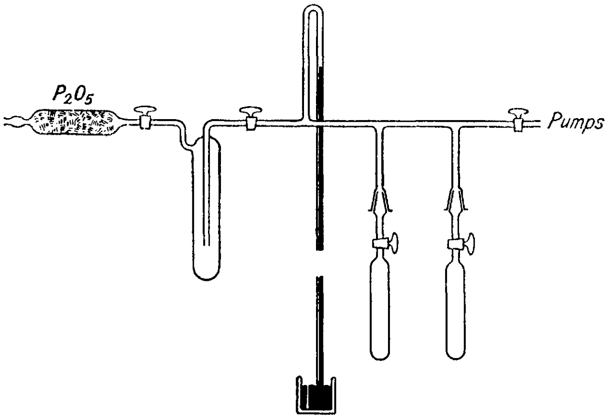


Table I.

Vapour Pressure of Carbonyl Selenide.

Bath.	Temp.	T.	P.	$\log_{10} P$.	$1000/T$.
$COMe_2$	−95°	178·0°	1·00	0·000	5·62
$CH_3{\cdot}CO_2Et$	−83·4	189·6	2·31	0·364	5·27
$CHCl_3$	−63·3	209·7	9·12	0·960	4·78
PhCl	−45·5	227·5	25·47	1·389	4·39
PhBr	−30·6	242·4	50·50	1·703	4·12
CCl_4	−22·9	250·1	72·29	1·859	4·00

(b) *The Decomposition of Carbonyl Selenide.*—When carbonyl selenide is passed through a heated tube, a sublimate of selenium is formed in the cooler portions of the tube, and conversely, carbonyl selenide is formed by the passage of carbon monoxide over heated selenium. Pearson and Robinson (*loc. cit.*) found that if the selenium was maintained at 500° the issuing gas contained 3·6% by volume of carbonyl selenide and at this temperature there is clearly an equilibrium $COSe \rightleftharpoons CO + Se$ with a concentration of carbonyl selenide somewhere near 3·6%. When the temperature is lowered, the equilibrium will be driven far over to the side of carbon monoxide and selenium, as the equilibrium constant will decrease and the concentration of the selenium vapour will fall off rapidly with temperature. Between our working temperatures of 120° and 140° the amount of carbonyl selenide formed cannot be detected, and one is concerned solely with its decomposition into carbon monoxide and selenium.

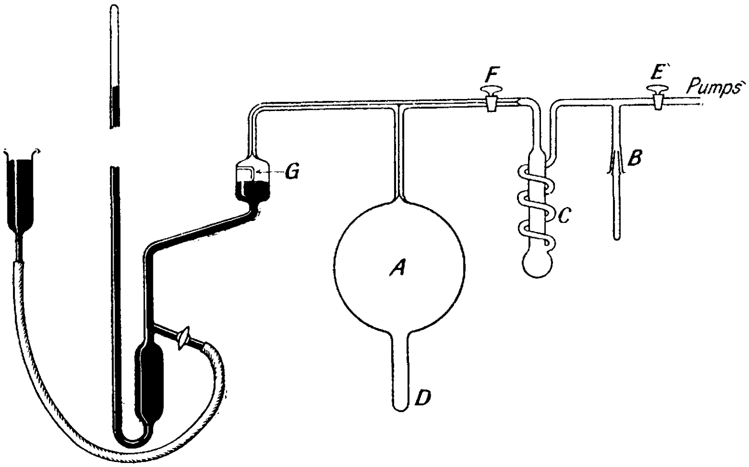
The apparatus used for following the decomposition is shown in Fig. 2. At the commencement of an experiment carbonyl selenide was transferred from the storage system to the reaction bulb A, through the standard ground-glass joint B, which at other times was closed by the taper as shown in the figure. After decomposition had proceeded for a given time, the contents of the bulb were slowly pumped off through the spiral C which was immersed in liquid nitrogen. This trapped the unchanged carbonyl selenide but allowed the carbon monoxide to be pumped away. Ten minutes' evacuation through a diffusion pump backed by a Hyvac pump sufficed to remove all the carbon monoxide, and, after the tap E had been closed, the carbonyl selenide could be condensed back into the tube D by cooling it with liquid air and allowing C to warm. Tap F was closed, and the pressure of the residual carbonyl selenide was measured by adjusting the reservoir so that the mercury level was just brought on to the small glass pointer G. The height between the mercury levels was then measured with the cathetometer. During the decomposition the mercury was pushed up to a fixed mark in the capillary tube so that all the carbonyl selenide was in the reaction bulb. This also served to keep clean the glass and mercury in the neighbourhood of the pointer so that later readings could be made without difficulty.

It is clear that the decomposition took place at a somewhat higher pressure than that measured, the true pressure, p, being 1·014 times the former when the room temperature was 20°.

The bulb *A* was surrounded by a heating bath of glycerol which had a gas thermoregulator and a stirrer bolted to the side so that the whole could be removed easily when the carbonyl selenide was being condensed back into the tube *D*.

The initial decomposition was on the clean glass bulb which had been baked out in vacuum. The glass was soon covered with an opaque film of selenium but the reaction was still very rapid. In 15 days it had fallen to one-hundredth of its initial value and thereafter there was no further systematic decrease, but a large fluctuation in the value of *k* about its mean value.

FIG. 2.



For a considerable time it was impossible to prevent or to discover the cause of these fluctuations, but it was obvious that the reaction was heterogeneous and extremely sensitive to slight changes in the surface. A clue was provided by the observation that after standing in vacuum at 130° over a week-end more decomposition took place on the surface than when it had only rested overnight, showing that the catalytic activity changed with time after the formation of the surface. To overcome these changes the reaction was allowed to proceed day and night, and was only interrupted for the short time required to pump off the carbon monoxide and to measure the decrease in pressure. The final pressure of one determination thus became the initial one of the next. Table II, in which p_0 is the initial pressure and *t* the time, shows that consistent results were obtained in this way. Determinations 1 and 2 are high, as no decomposition had taken place on the surface for the preceding 48 hours.

TABLE II.

Temperature 130°.

Detmtn. No.	p_0, cm.	t, mins.	$10^4\Delta p/\Delta t$.	$k \times 10^6$.	Max. error.
1	15·52	200	11	72	±8
2	15·30	1130	6·8	46	2
3	14·53	300	5·3	37	6
4	14·37	1110	5·5	37	2
5	13·76	300	4·7	35	6
6	13·62	1070	4·7	36	±2
7	13·105	300	4·7	35	5
8	12·965	1080	4·5	35	2
	12·485 (final press.)				

k (by summation of Nos. 3—8) = $(1/4160) \log_e 14{\cdot}53/12{\cdot}485 = 36{\cdot}5 \pm 0{\cdot}05 \times 10^{-6}$.

At this time the apparatus had to be left for 6 weeks, after which a further series of readings was made at 130°. Initially, $k = 376 \times 10^{-6}$, but the rate of decomposition decreased rapidly until after 6 days $k = 35 \times 10^{-6}$ and the series of results shown in Table III was then obtained. At pressures above 16 cm. the decomposition was unimolecular, but at lower pressures the constant *k* increased, showing that the reaction was proceeding more rapidly than expected. Determinations 4, 9, 14, and 19 were extended over 2 days in an attempt to obtain larger pressure changes and therefore greater accuracy. Unfortunately, the accumulation of the resulting carbon monoxide retarded the reaction and, as can be seen, the results were low. In subsequent work short runs were used, so the carbon monoxide could be pumped away before its effect

TABLE III.

	Temp. = 130°.			Temp. = 120°.		
Detmtn. No.	p_0, cm.	t, mins.	$k \times 10^6$.	p_0, cm.	t, mins.	$k \times 10^6$.
1	33·015	300	26	28·145	1110	27
2	32·76	1080	33	27·315	300	26
3	31·61	300	33	27·10	1070	28
4	31·295	2860	31·7	26·295	—	—
5	28·58	—	—	18·91	300	28
6	21·41	1100	31	18·745	1100	26
7	20·695	300	33	18·21	—	—
8	20·49	1100	31	13·565	1080	28
9	19·805	3000	29·5	13·165	300	31
10	18·13	—	—	13·045	1100	27
11	11·655	300	44	12·665	—	—
12	11·50	1060	45	7·96	1100	24
13	10·95	300	43	7·75	300	39
14	10·81	2860	39·1	7·66	1160	26
15	9·665	—	—	7·435	—	—
16	5·39	300	40	3·23	1080	25
17	5·325	1100	54	3·145	300	40
18	5·02	300	40	3·10	1100	28
19	4·96	3000	46·4	3·005	—	—
20	4·315	—	—	—	—	—

became appreciable. Further series of experiments were made at 120° and 140° and the results are given in Tables III and IV respectively.

TABLE IV.

Temperature 140°.

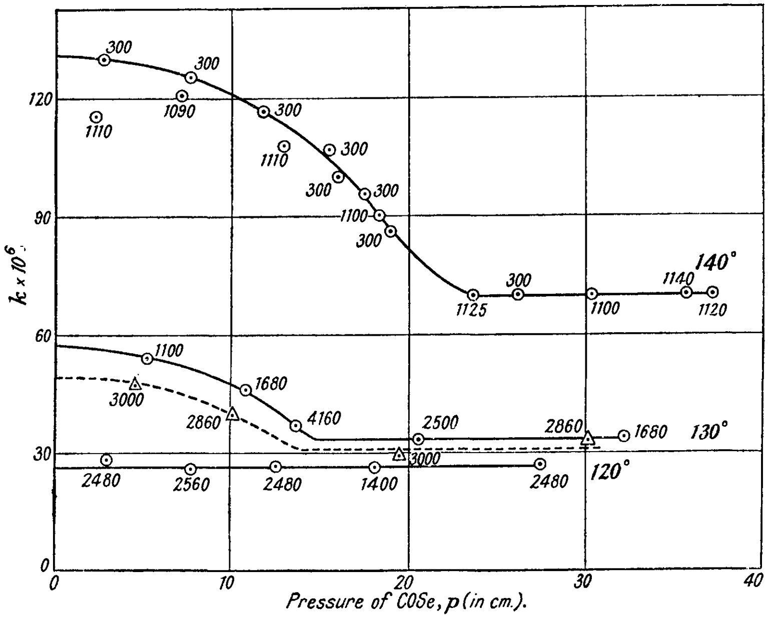
p_0, cm.	Final press., cm.	Mean press., cm.	t, mins.	$10^5\Delta p/\Delta t$.	$k \times 10^6$.	p_0, cm.	Final press., cm.	Mean press., cm.	t, mins.	$10^5\Delta p/\Delta t$.	$k \times 10^6$.
36·45	33·715	35·08	1120	244	69	15·54	15·08	15·34	300	153	100
35·85	33·15	34·50	1140	237	69	15·525	15·04	15·28	300	162	106
30·415	28·20	29·31	1100	201	69	13·42	11·90	12·66	1110	137	108
26·305	25·77	26·04	300	178	68	11·90	11·485	11·69	300	138	118
23·74	21·94	22·84	1125	161	70	7·485	7·205	7·345	300	93	127
19·04	18·545	18·79	300	165	88	7·205	6·31	6·76	1090	82	121
18·545	16·80	17·67	1100	159	90	2·975	2·86	2·92	300	38	131
17·61	17·12	17·36	300	163	93	2·86	2·515	2·69	1110	31	116

The results of all the determinations are collected together in the graph in Fig. 3, where the arithmetic means of the initial and final pressures of decomposition are plotted against the corresponding values of k calculated on the assumption that the unimolecular law was followed. It will be seen that at higher pressures k is constant at all three temperatures, but that at 130° and 140° it increases rapidly below certain critical pressures. The figures by the side of the points refer to the time in minutes of the decomposition, or summed decompositions, for which they are calculated. The lines are drawn preferentially through the higher points, which correspond with short periods of decomposition at 140°, where there has been little reaction and consequently only a small amount of the inhibiting carbon monoxide formed.

DISCUSSION.

It has been shown that the decomposition is extremely sensitive to changes in the selenium, which, except under special conditions, is not a constant catalytic surface. In view of the known allotropic complexity of selenium this is not surprising, as it might be expected that the element first deposited from the carbonyl selenide would go through one or more transformations before reaching inner equilibrium. This is supported by the deposition of red selenium observed when the carbonyl selenide is rapidly decomposed; *e.g.*, near the hot glass when a bulb containing the gas is sealed off. The red form slowly turns black and then appears identical with the black film observed in the decomposition bulb. It can therefore be postulated that the selenium is first deposited in a form indicated by Se-I and that this changes into a more stable variety, Se-II, at a rate depending on the temperature and on the quantity present. Hence, there can be two forms of selenium in the surface and they have different catalytic activity towards carbonyl selenide, the form Se-II having the greater effect. For the higher pressures at 130° and 140° the amount of Se-I deposited by the carbonyl selenide is greater than that which changes into Se-II in the same time; hence the surface exposed to the gas is exclusively Se-I and the reaction is unimolecular. At a certain pressure the rate of change Se-I $\longrightarrow$ Se-II on the bulb equals the rate of decomposition COSe $\longrightarrow$ CO + Se, and Se-II can appear in the surface for the first time. This causes the unimolecular constant to begin to increase, but not $\Delta p/\Delta t$, which remains nearly constant for a time as more Se-II appears and the effect of its greater catalytic activity is manifest. It is clear that where decomposition proceeds on two surfaces a condition of equilibrium is set up, in which the amount of Se-I deposited equals the amount changing into Se-II in the same time, thus giving a constant surface at a given pressure. When decomposition is arrested, the change Se-I $\longrightarrow$ Se-II can still go on, so the next decomposition is on a surface containing more Se-II and therefore gives the high value of k shown at the beginning of Table II. With intermittent working, the nature of the surface at the beginning of an experiment will depend on the extent of the previous decomposition and the time that has since elapsed, and consequently consistent results cannot be obtained.

FIG. 3.



If k_1 and k_2 are the velocity constants on the Se-I and the Se-II surface respectively, and if the rate of transformation of Se-I into Se-II is proportional to k_3 times the percentage of Se-I in the surface, it can be shown that the rate of decomposition $\Delta p/\Delta t$ is connected with the pressure p by the following relationship :

$$\Delta p/\Delta t = k_2 p/[1 + p(k_2 - k_1)/k_3] = k_2 p/(1 + K_2 p) \quad . \quad . \quad . \quad (1)$$

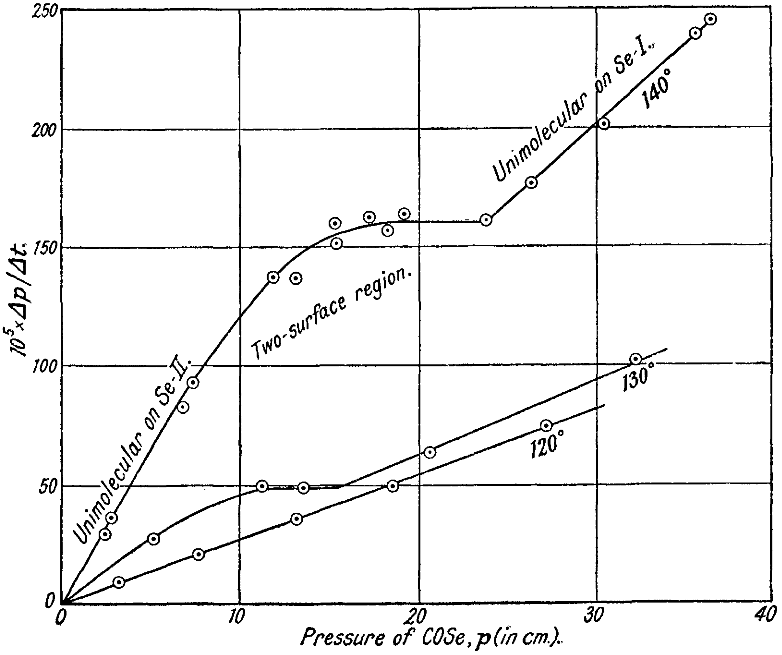
The second form of the expression is identical with Langmuir's well-known equation for a reaction with intermediate adsorption. A heterogeneous gas reaction, in which the catalytic adsorption was of the above type, would show a unimolecular reaction at low pressures and would tend to a zero-order reaction as the pressure increased. Similar effects are shown in the present case in the two-surface region as seen in Fig. 4, where the curve has a constant slope at low pressures and a horizontal portion at medium pressures, but the subsequent return to a unimolecular reaction on Se-I surfaces at still higher pressures shows that the results cannot be interpreted in terms of the Langmuir equation alone.

Values of k_2 and K_2 in equation (1) can be evaluated by the substitution of experimental results: k_2 is the slope of the $\Delta p/\Delta t$—p curve when p approaches zero, and at 140° is equal to 125×10^{-6}; then, since $\Delta p/\Delta t = 161 \times 10^{-5}$ when $p = 23{\cdot}7$ cm., $K_2 = 0{\cdot}038$. These values of K_2 and k_2 enable $\Delta p/\Delta t$ to be calculated from, and plotted against, p. The resulting curve, although of the right form, does not bend round so sharply as the experimental one, and cannot be made to fit it. The deviation can be attributed to the conditions for the transformation Se-I $\longrightarrow$ Se-II being different from those postulated, the change from 100% Se-I to 100% Se-II in the surface apparently occurring between the pressures 10—23·7 cm. It is possible to calculate the percentage y of Se-I in the surface from the equation

$$\Delta p/\Delta t = k_1 py + k_2 p(1 - y)$$

This has been done by taking $k_2 = 125 \times 10^{-6}$ and $k_1 = 69 \times 10^{-6}$, and when the resulting values of y are plotted against p the points, although rather scattered, appear to lie on a straight line from 100% Se-II at 10 cm. to 100% Se-I at 23·7 cm. If this is so, the following modification of the formula enables $\Delta p/\Delta t$ to be accurately calculated from p in the two surface region:

FIG. 4.



$$\Delta p/\Delta t - 0{\cdot}00121 = 0{\cdot}000125(p - 10)/[1 + 0{\cdot}239(p - 10)]$$

Consequently, the decomposition at 140° may proceed according to three processes. Between $p = 0$ and $p = 10$ cm., and when p is greater than 23·7 cm., it is unimolecular on the Se-II and the Se-I surface respectively, whilst between 10 and 23·7 cm. it occurs on both surfaces simultaneously.

The allotropy of selenium is not sufficiently understood to enable a definite correlation with the above theory to be made. Nevertheless, the hypothesis is not out of harmony with the work of Briegleb (*Z. physikal. Chem.*, 1929, **144**, 321), who showed that the allotropy is to be attributed solely to dynamic equilibrium between the molecular species Se_2 and Se_1. The two forms called Se-I and Se-II above are probably the α- and the β-variety of monoclinic selenium, both being pseudo-equilibrium mixtures. These forms revert to the stable grey metallic form of the element, and it is this which appears ultimately in the reaction bulb. The very high value of k, 376×10^{-6}, obtained after 6 weeks' interval during which no decomposition took place, is for the reaction on this surface. Consequently, the reaction velocity is much greater on the grey form than on the β-monoclinic variety, on which it is again greater than on the α-form. At the lowest pressure at which we have worked the grey selenium does not appear on the surface when decomposition is continuous; instead, the surface is Se-II (or Se_{β}) on which the unimolecular constant k_2 approaches a constant value that is larger than the corresponding constant for the Se-I (or Se_{α}) surface.

The carbon monoxide formed by the decomposition has an appreciable retarding effect at lower pressures as shown in Fig. 3, where the broken curve joins the values of k obtained when the carbon monoxide accumulates in the system. The effect is greater the lower the pressure, and at high pressures is small. This indicates that the carbon monoxide is strongly adsorbed on the Se-II only, where it displaces carbonyl selenide and reduces the decomposition rate. The effect of the carbon monoxide is greater at higher temperatures; at 140° it is measurable after 1000 minutes' decomposition at low pressures, whilst at 120° its influence cannot be detected.

The k–p curve at 120° does not show the characteristic break exhibited by the others, the reaction being unimolecular over the entire range examined. The values of k at zero pressure, by extrapolation from the curves in Fig. 3, are 27·5, 59·5, and 131, giving a temperature coefficient of 2·18 for each 10° rise. Therefore the surface at 120° over the *whole range* must be the same as that at zero pressure at 130° and 140°, *i.e.*, it is Se-II. The temperature coefficient enables a heat of activation to be calculated from the Arrhenius equation; its value is 24,600 cals./g.-mol.

The sudden break in the k–p curve takes place at a higher pressure at 140° than at 130°. This means that the rate of change of Se-I into Se-II is accelerated by this temperature increase to a greater extent than the decomposition of carbonyl selenide. The values of $\Delta p/\Delta t$ at these two points, *viz.*, 0·00161 and 0·00053 are measures of the rates of change of Se-I into Se-II, since in each case there is the same amount of Se-I, *viz.*, just sufficient to cover the surface completely. The temperature coefficient for the transformation Se-I $\longrightarrow$ Se-II is consequently 3·04.

Further work is in progress on the allotropic transformation of the selenium surfaces, which may establish that they are identical with the α- and β-modifications investigated by Briegleb. It is considered, however, that the kinetic data given prove the existence of dynamic allotropy in the surface, and that this constitutes the first investigated example of a gaseous decomposition which is dependent on a consecutive reaction in the catalytic surface.

SUMMARY.

The vapour pressure of carbonyl selenide has been redetermined and errors recorded in the literature corrected.

The decomposition of carbonyl selenide on selenium has been studied at 120°, 130°, and 140°. Two forms of selenium may be found on the surface which have been designated Se-I and Se-II. The decomposition is unimolecular on both allotropes but, under certain conditions, they may both be present together, and the reaction then appears complex. It can be interpreted in terms of the two unimolecular reactions and the percentages of Se-I and Se-II present in the surface.

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