The maintenance of the high pressure rate over the pressure range studied can be theoretically accounted for if the molecule is assumed to have a diameter of 8×10^{-8} cm. and to contain 14 classical oscillators.

The possible equilibrium between phosgene, carbon monoxide and chlorine was not found to occur as a result of the reaction, the sole product of the decomposition being phosgene.

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The Effect of Gaseous Impurities on the Radiochemical Combination of Carbon Monoxide and Oxygen

BY CHARLES ROSENBLUM

Part of the recent work on the carbon monoxide oxidation under the influence of radon[1] involved a study of the effect of certain gaseous impurities possibly occurring in traces in the reactants as a result of the methods employed for their preparation. These foreign substances were water vapor, formic acid vapor and gaseous nitrogen.

The formic acid was prepared by reduced pressure distillation[2] in the presence of phosphorus pentoxide, and saturation of a $2CO:1O_2$ mixture was effected at 21.3°. Another sample of the reaction mixture was saturated with water vapor at 21.5°. A measured volume of tank nitrogen, purified by passing through a train containing, besides a liquid air trap, tubes of fused potassium hydroxide, sublimed phosphorus pentoxide and yellow phosphorus, was added to a third quantity of reactants. The gas mixtures so prepared were confined with radon in small spherical vessels[3] and the progress of the reaction followed manometrically.

Table I shows the reaction in gases wet with water vapor. Here $e^{-\lambda t}$ is the fraction of radon left after time t, E_0 is the initial amount of radon in curies, $P_{2CO + 1O_2}$ is the partial pressure of dry reactants, D is the diameter of the reaction vessel, and $(k\mu/\lambda)''_{\text{corr.}}$ is the velocity constant corrected for the catalytic efficiency of carbon dioxide and for the effect of recoil atoms.[1]

From the inverse square of diameter law[4] the velocity constant in a sphere of this size should be about 31,[1] which may be considered in agreement for experiments of this kind. It then appears that water vapor has little effect on the radiochemical carbon monoxide oxidation. That water vapor has a negligible effect is in accord with its radiochemically inert nature.[5]

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[1] Lind and Rosenblum, *Proc. Nat. Acad. Sciences*, **18**, 374 (1932).

[2] Jones, *J. Soc. Chem. Ind.*, **38**, 362T (1919).

[3] Lind and Bardwell, THIS JOURNAL, **47**, 2675 (1925).

[4] Lind, *ibid.*, **41**, 531 (1919).

[5] Duane and Scheuer, *Le Radium*, **10**, 33 (1913).

TABLE I

THE INFLUENCE OF WATER VAPOR

$D = 1.958$ cm.; $E_0 = 0.0451$ curie radon

$e^{-\lambda t}$	$P_{2CO + 1O_2}$, mm.	$(k\mu/\lambda)''_{\text{corr.}}$
1.0000	740.1	
0.9705	700.2	34.0
.9277	647.5	32.6
.8869	602.2	31.2
.8479	564.6	28.6
.8106	530.5	28.5
.7691	492.7	30.0
.7243	456.6	28.0
.6771	423.0	26.2
.6329	393.0	26.3
.5872	363.4	26.5
.5387	334.0	26.2
.4923	308.8	24.8
.3787	255.1	24.0
.3358	235.2	25.1
.2933	218.7	23.0
.2507	202.0	23.7
.2042	183.7	24.5
.1532	159.4	31.5
.0606	122.1	28.4
	Av.	27.5

TABLE II

THE EFFECT OF FORMIC ACID VAPOR

$D = 1.795$ cm.; $E_0 = 0.0425$ curie radon

$e^{-\lambda t}$	$P_{2CO + 1O_2}$, mm.	$(k\mu/\lambda)''_{\text{corr.}}$ I	II
1.0000	711.3		
0.9560	686.1	15.7	80.7
.9105	631.8	34.3	38.7
.8672	585.7	32.6	37.0
.8278	549.9	29.2	33.9
.7911	517.3	30.1	34.7
.7509	483.0	30.2	35.5
.6977	438.3	31.7	37.3
.6497	402.1	30.5	36.3
.5890	359.1	30.8	37.4
.5273	315.9	33.0	40.6
.4671	285.3	25.8	32.4
.4026	247.9	31.9	39.2
.3435	216.1	32.0	40.7
.2882	189.3	31.3	42.8
.1992	145.3	35.3	49.0
.1152	102.3	42.3	63.3

The effect of formic acid vapor is given in Table II.

The corrected velocity constants in column I are calculated in the usual manner directly from the pressure of reactants as indicated by the total pressure drop. The low constant for the first interval shows that formic acid is being decomposed, the formation of its decomposition products producing a pressure increase which masks the disappearance of carbon monoxide and oxygen.

It is impossible to say for certain what these decomposition products may be. The simplest assumption is either hydrogen and carbon dioxide or water vapor and the monoxide. However, supposing the formic acid to yield twice its volume in decomposition products, the partial pressure of reactants will be considerably less than was calculated simply from the total pressure drop. The result of this recalculation, confining the entire side reaction to the first interval, is shown in column II. These constants are somewhat higher than the expected value of 37. However, it is apparent that the sole effect of formic acid vapor is to mask the main reaction in its earlier stages, and this only when present in appreciable quantities.

The effect of nitrogen was interesting in that it is an excellent ionic catalyst[6] as contrasted with the inefficient carbon dioxide. Furthermore,

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[6] Lind and Bardwell, THIS JOURNAL, **48**, 1575 (1926).

this system involved the simultaneous effect of two radiochemical catalysts, a situation hitherto found only in the case of catalysis of the carbon monoxide oxidation by the relatively inefficient argon. In the following experiment, a mixture containing 33.8% nitrogen was used.

TABLE III

THE EFFECT OF NITROGEN

$D = 2.006$ cm.; $E_1 = 0.0342$ curie radon

$e^{-\lambda t}$	P_{2CO+1O_2}, mm.	$(k\mu/\lambda)'_c$	$(k\mu/\lambda)'_{corr.}$		$(k\mu/\lambda)''_{corr.}$	
		I	II	III	IV	V
1.0000	727.1					
0.9705	662.3	92.4	78.6	52.7	51.0	41.0
.9394	591.6	106.0	88.9	57.7	61.2	40.9
.9105	535.2	101.3	83.4	52.5	40.7	42.0
.8803	477.9	109.6	88.4	53.8	51.9	41.1
.8511	426.9	112.9	88.9	52.3	50.3	39.3
.8136	365.0	122.0	93.3	52.4	50.3	38.8
.7658	299.0	121.9	88.2	46.7	44.7	34.4
.7321	254.3	140.3	99.0	49.2	46.9	34.6
.6925	207.0	151.8	99.6	46.4	44.1	32.6
.6436	154.7	174.0	103.6	46.4	44.0	31.9

Inspection of velocity constants indicates unmistakably the efficient nature of nitrogen as an ionic catalyst. Column I shows the velocity constant $(k\mu/\lambda)'_c$ calculated from total pressure drop disregarding ionization on the catalysts. Column II corrects for the catalytic effect of carbon dioxide, assuming its efficiency to be 14.5%.[1] Attributing in addition 100% efficiency as a catalyst to the nitrogen, column III is obtained. Making proper correction for the effect of recoil atoms column IV is calculated from column III.

Since the corrected constants $(k\mu/\lambda)''_{corr.}$ should be about 31, we are evidently faced with a significant velocity increase. The simplest manner of accounting for this increase is to assume an enhanced efficiency of the ionization falling on the carbon dioxide when in the presence of such an efficient catalyst as nitrogen. Assuming an efficiency of 30% for carbon dioxide, column V is obtained, which is a decided approach toward a correct representation of the reaction velocity.

A mechanism for such an unexpected effect cannot be suggested because the bulk of the sensitized radiochemical effects studied have involved only single catalysts. The result in the case here reported seems to indicate transfer of ionization by the efficient catalyst (nitrogen) not only to reactants but as well to the less efficient catalyst (carbon dioxide).

Summary

The effect of water vapor, formic acid vapor and nitrogen on the combination of carbon monoxide and oxygen in the presence of radon was studied. Water vapor had a small retarding effect on the reaction. For-

mic acid vapor did not directly affect the velocity of the main reaction, tending only to mask its course in the early stages by undergoing decomposition. Nitrogen had an extreme accelerating influence on the oxidation, which could be explained by an increase in the catalytic efficiency of carbon dioxide from 14.5 to 30%, in addition to the 100% efficiency of nitrogen.

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An Anomalous Decomposition of Ozone in the Presence of Chlorine

BY LAWRENCE J. HEIDT, GEORGE B. KISTIAKOWSKY AND GEORGE S. FORBES

Several investigators[1] of the decomposition of ozone in the presence of chlorine have reported that the quantum yield, ϕ (ozone molecules decomposed per quantum absorbed), is 2.0 ± 0.2 in spectral regions where chlorine only absorbs, that the light reaction is nearly independent of the concentrations, and that the dark reaction[2] is relatively small at room temperature. The dark reaction has since been studied at 35 and 60° by Hamann and Schumacher.[3] The photolysis has been used as an actinometer.[4] The observations by Allmand and Spinks[1a] indicated that the course of the reaction was decidedly irregular. We undertook its further study at lower temperatures using an apparatus[5] recently devised for referring ϕ in gas reactions to uranyl oxalate as an actinometer. Attention is called to the stringent precautions there described regarding temperature control and pressure measurement. A second paper of Allmand and Spinks[6] stated, as we had noticed in the meantime, that the dark reaction and wall effects were important, and expressed regret that these had not been further studied. None the less, they still viewed their reaction as essentially photochemical. These workers found that with O_3 greater than 35% and Cl_2 about 1%, values of ϕ up to 59 could be obtained; these values decreased as the light intensity, I, increased, the reaction rate being approximately proportional to $I^{1/2}$; the 10° temperature coefficient of the rate under these conditions was about 1.5, as compared with 1.0 when the chlorine percentage was higher, ϕ smaller, and the rate proportional to I.

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[1] For a review of the literature see (a) Allmand and Spinks, *J. Chem. Soc.*, 1652 (1931); (b) Taylor, *J. Phys. Chem.*, **34**, 2082 (1930); (c) Schumacher and Wagner, *Z. physik. Chem.*, [B] **5**, 199 (1929); (d) Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Green and Co., New York, 1929, pp. 601–605; (e) Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, 1932, pp. 254–262.

[2] Bodenstein, Padelt and Schumacher, *Z. physik. Chem.*, [B] **5**, 209 (1929).

[3] Hamann and Schumacher, *ibid.*, [B] **17**, 293 (1932).

[4] Cremer, *ibid.*, **128**, 285 (1927).

[5] Forbes, Kistiakowsky and Heidt, THIS JOURNAL, **54**, 3246 (1932).

[6] Allmand and Spinks, *J. Chem. Soc.*, 599 (1932).