Summary

1. Of the five metals studied in the present work, *viz.*, ruthenium, osmium, iridium, palladium and platinum, only palladium gave satisfactory polarographic steps.

2. Palladium complexes in general are reducible at the dropping electrode giving one step which corresponds to direct reduction of Pd^{II} to Pd. Various supporting electrolytes which form complexes with the metal are suitable for its analytical determination.

3. In complexes of palladium with amines, the half-wave potential becomes more negative with increasing basic strength of the amine, *i. e.*, the complexes become more resistant to reduction. At the same time the reduction becomes less reversible.

4. The relative stabilities of the complex cyanides of Group VIII are discussed in the light of their polarographic behavior.

SYDNEY, AUSTRALIA RECEIVED DECEMBER 27, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Effect of Nitric Oxide upon the Biacetyl Promoted Thermal Decompositions of Acetone and Acetaldehyde

BY CHARLES H. KLUTE[1] AND W. D. WALTERS

Earlier studies[2,3] have shown that nitric oxide often has a considerable effect upon the thermal decompositions of organic compounds. Verhoek[2] observed that nitric oxide catalyzed the thermal decompositions of acetaldehyde, trichloroacetaldehyde, and chloroform. Later Staveley and Hinshelwood[3a] and also other investigators[3b,c] demonstrated that nitric oxide exerts an inhibiting influence on the decompositions of ethers, hydrocarbons, and certain aldehydes.

Subsequent investigations have indicated that nitric oxide may not always be a satisfactory inhibitor. Although it was observed that nitric oxide did not inhibit the thermal decompositions of acetone and acetaldehyde,[3a] Rice and Polly[4a] found that the rates of pressure increase in these decompositions can be considerably reduced by the addition of propylene. Rice and Polly observed also that ethyl nitrite, which produces nitric oxide upon decomposition, has only a relatively small effect upon the oxygen promoted decomposition of acetaldehyde occurring during the first few seconds at 500°. Moreover, nitric oxide does not inhibit the hydrogen sulfide catalyzed acetaldehyde decomposition.[4b] In the decomposition of *n*-butane induced by ethylene oxide, Steacie and Folkins[5] showed that not all of the chains are stopped by nitric oxide.

Recently Smith and Hinshelwood[6] by analyzing chemically for undecomposed aldehyde have confirmed the fact that the acetaldehyde decomposition is much slower in the presence of propylene than in the presence of nitric oxide. Concerning this inhibition by propylene Morris[7] has concluded that the inhibition involves only an induced decomposition which is superimposed upon the true unimolecular process. However, irrespective of differences in interpretation of the propylene inhibition it is significant that in the presence of certain carbonyl compounds nitric oxide may not be an efficient inhibitor. Therefore, in order to investigate further the effectiveness of nitric oxide as a chain inhibitor, a study of the influence of nitric oxide upon the biacetyl promoted decompositions of acetone and acetaldehyde was undertaken.

Experimental

Apparatus and Method.—The reaction vessel, a cylindrical Pyrex bulb, 61 × 135 mm., was contained in a steel cylinder, and the furnace was heated electrically by the use of Nichrome resistance wire wound around the asbestos-covered steel cylinder. The temperature of the furnace was automatically controlled as in an earlier study,[8] and a chromel–alumel thermocouple connected to a potentiometer was used to measure the temperature. During a run the temperature was maintained constant to within ±0.3°, and the accuracy of the temperature measurements should be at least ±1 since the chromel–alumel thermocouples, standardized at the sulfur boiling point,[9] were replaced frequently.

In the case of the acetaldehyde decomposition it has been observed that traces of oxygen accelerate the decomposition and that the rate of the decomposition is faster in a reaction vessel freshly cleaned with nitric acid or in a vessel evacuated exhaustively.[10] However, Leifer and Urey[11] found that only by oxygen treatment followed by diffusion pumping could the walls of the reaction vessel be freed completely of the nitric oxide used in a previous experiment. Therefore, in the present investigation the following procedure was adopted. Runs were made in the following order: (a) acetaldehyde, (b) acetaldehyde and biacetyl, (c) acetaldehyde, biacetyl, and nitric oxide. Before the rate of decomposition of pure acetaldehyde was

---

[1] Fellow of the Sherman Clarke Fund for Chemical Research, University of Rochester.

[2] Verhoek, *Trans. Faraday Soc.*, **31**, 1521, 1533 (1935).

[3] (a) Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **154A**, 335 (1936); **159A**, 192 (1937); *J. Chem. Soc.*, 1568 (1937); (b) Hobbs and Hinshelwood, *Proc. Roy. Soc.* (London), **167A**, 439, 447 (1938); (c) Echols and Pease, THIS JOURNAL, **61**, 1024 (1939).

[4] (a) Rice and Polly, *J. Chem. Phys.*, **6**, 273 (1938); (b) Roth and Rollefson, THIS JOURNAL, **64**, 1707 (1942).

[5] Steacie and Folkins, *Can. J. Research*, **17B**, 105 (1939).

[6] Smith and Hinshelwood, *Proc. Roy. Soc.* (London), **180A**, 237 (1942); similar work with acetone, *ibid.*, **183A**, 33 (1944).

[7] Morris, THIS JOURNAL, **66**, 584 (1944).

[8] Gantz and Walters, *ibid.*, **63**, 3412 (1941).

[9] Mueller and Burgess, *Bur. Standards Sci. Pap.*, **15**, 163 (1919), S 339.

[10] Letort, *J. chim. phys.*, **34**, 265, 355, 423 (1937).

[11] Leifer and Urey, THIS JOURNAL, **64**, 995 (1942).

measured for each set of runs, the reaction vessel was flushed a few times with air, followed by several charges of acetaldehyde which were allowed to decompose in the reaction vessel. After each charge the reaction vessel was evacuated to a vacuum of 10^{-4} mm. It was felt that the procedure adopted would give more reproducible results than one in which various substances were allowed to accumulate on the surface. The same procedure was followed with acetone, but the acetone decomposition is not so susceptible as the acetaldehyde decomposition to traces of oxygen and effect of surface.

A comparison with recently summarized values[7] for the rate of decomposition of purified acetaldehyde, not hydroquinone treated, shows that the present results are in agreement with the data of Morris[7] and Smith,[12] but somewhat higher than those of Letort.[10] At 494° and 302 mm. initial pressure the rates obtained by Morris, Smith, and Letort were 12.0, 14.3, and 8.5 mm. per min., respectively. These values as well as those in the present experiments have been corrected to 494° on the basis of an activation energy of 46 kcal. The average of the initial rates at 494° from the present study, corrected to 302 mm. by using the equation $-dx/dt = kx^{1.5}$ was found to be 11.5 mm. per min., or if corrected by the use of $-dx/dt = kx^{1.6}$ the average was 12.1 mm. per min. Some of the difference between the present results and those of Letort may be due to the fact that the surface of his reaction vessel was probably kept in a more highly poisoned condition. However, it is to be noted that Morris observed that the treatment of acetaldehyde with hydroquinone reduces the rate of decomposition to a value slightly lower than that found by Letort. As a result it was indicated that the hydroquinone removes an impurity which initiates a portion of the decomposition. The possibility that hydroquinone introduces an inhibitor was not completely excluded, but it is probably rather remote in view of the agreement between the results of Morris and Letort. Nevertheless, as the discussion indicates, the conclusions of the present investigation will remain the same regardless of whether the rate before or the rate after hydroquinone treatment is regarded as the true rate.

In most of the runs in which nitric oxide was used, the nitric oxide was introduced into the reaction vessel and then the material under investigation was added, since apparently this was the procedure used by Hinshelwood and his co-workers in their investigations. In order to determine whether the results were influenced by the method of introduction of nitric oxide, a number of runs were made with mixtures of biacetyl, acetone, and nitric oxide which had been allowed to mix thoroughly before introduction into the reaction vessel. The results obtained were in agreement with those observed in the runs in which nitric oxide was introduced directly into the reaction vessel followed by the mixture of organic compounds. Experiments involving acetaldehyde in the place of acetone were carried out in a similar manner.

Materials.—Nitric oxide was prepared by adding a solution of potassium nitrite dropwise to a solution of ferrous sulfate and sulfuric acid. The nitric oxide was passed first through a scrubbing column containing concentrated sulfuric acid and then through a similar column containing 50% potassium hydroxide. The gas was dried by the use of calcium chloride and phosphorus pentoxide drying columns. After the nitric oxide had been passed through two traps at −80°, it was stored in evacuated gas storage bulbs. Prior to use in the thermal reactions, the nitric oxide was condensed and then distilled under vacuum to insure its purity. In addition, before each use with acetaldehyde or acetone the inhibiting influence of the nitric oxide sample was verified by testing its effectiveness in inhibiting the dimethyl ether decomposition.

Biacetyl from Eastman Kodak Company was purified as in an earlier investigation.[13] Acetone, Merck Reagent, dried over calcium sulfate was fractionated three times in an all-glass still through a 60 cm. vacuum-jacketed column, the middle two-thirds fraction being retained in each distillation. The final middle fraction (b. p. 55.1° at 739.7 mm.) was distilled directly into the storage bulb. Two samples of acetaldehyde were prepared: for the first, acetaldehyde from Eastman Kodak Company (highest grade) dried over calcium sulfate was fractionated three times as in the case of acetone above, outgassed seven times at −80°, and vacuum-distilled twice; for the second, acetaldehyde from Kahlbaum (reagent grade) was outgassed four times at −80° and then vacuum-distilled four times, half of the material being removed as top and bottom fractions. Between successive outgassings the acetaldehyde was warmed to room temperature.

Dimethyl ether with a stated purity of 99.95% was obtained from the Ohio Chemical Company and was used without further purification.

Results and Discussion

Acetone.—The results of the experiments with mixtures of acetone, biacetyl and nitric oxide are summarized in Table I. As can be seen from $t_{12.5}$, the time for the pressure to increase 12.5%, or from ΔP_{10}, the pressure increase during the first ten minutes, the addition of a small amount of biacetyl promotes the decomposition of acetone. In three experiments at

TABLE I

EFFECT OF NITRIC OXIDE UPON THE PROMOTED DECOMPOSITION OF ACETONE

P_0 is the initial pressure of the acetone plus biacetyl. ΔP_{10} is given to the nearest 0.5 mm.

Temp., °C.	P_0, mm.	Ac_2, %	P_{NO}, mm.	ΔP_{10}, mm.	$t_{12.5}$, min.
523	159	0.0	0.0	14.5	14.1
523	157	.0	.0	14.5	14.0
522	173	.0	.0	15.5	14.1
523	159	.97	.0	38.0	3.2
523	162	1.00	.0	41.0	2.8
524	159	1.00	.0	39.5	2.9
523	159	1.01	.09	39.5	3.0
523	161	0.99	.48	39.0	3.2
523	170	.99	3.94	39.0	3.6
523	156	.99	5.9	34.0	4.0
523	157	.97	11.8	37.0	3.9
523	163	1.01	12.3	39.0	3.7
523	160	0.0	0.10	14.0	14.6
522	160	.0	.54	14.5	14.1
523	170	.0	4.2	22.0	9.6
523	161	.0	12.0	28.0	7.2
523	183[a]	.0	0.0	18.0	12.7
522	180[a]	.0	.0	16.5	13.5
522	161[b]	.0	.0	13.5	15.4
522	185[b]	.98	.0	43.5	3.2
522	177[a]	1.04	.0	42.5	3.1
522	185[b]	0.98	0.52	43.5	3.1
522	194[a]	1.04	4.8	43.5	3.7
522	187[b]	1.00	13.5	40.6	4.2
522	185[b]	0.0	0.56	15.3	15.9
522	192[b]	.0	15.8	31.2	7.6

[a] Experiments made at an earlier time in a different apparatus. [b] In experiments designated as *a* or *b* mixtures of acetone, biacetyl, and nitric oxide were introduced into the reaction vessel. In other cases nitric oxide was introduced first into the bulb followed by a mixture of acetone and biacetyl.

---

(12) Smith, *Trans. Faraday Soc.*, **35**, 1328 (1939).

(13) Walters, THIS JOURNAL, **62**, 883 (1940).

523° with (a) acetone, (b) acetone containing 1% biacetyl and (c) acetone containing 1% biacetyl in the presence of 5.9 mm. of nitric oxide, the ratios of the final pressure to the initial pressure were found to be the same ($P_f/P_0 = 2.2$, without dead space correction) within the limits of experimental error. None of the values differed more than 1% from the average of the three. Previously it has been found that the greater rate of pressure increase in the biacetyl promoted decomposition of acetone is accompanied by a greater rate of ketene formation.[14] These results indicate that pressure measurements may be used as a basis of comparison of the different runs since it appears that the major portion of the over-all reaction is essentially the same in the three cases, namely

$$CH_3COCH_3 = CH_4 + CH_2CO$$

the ketene being subject to further decomposition.

Since in other thermal decompositions small amounts of nitric oxide, 1 mm. or less, often produce almost the maximum inhibition, rate measurements were made in the presence of a small pressure of nitric oxide, but the results in Table I show that the biacetyl promoted decomposition proceeds at approximately the same rate with or without the addition of 0.1 or 0.5 mm. of nitric oxide. Even with larger amounts of nitric oxide the rate in the presence of biacetyl is always greater than that for acetone alone or for acetone plus nitric oxide, and it is evident that none of the various amounts of nitric oxide which were tried suppresses the biacetyl promoted decomposition of acetone to any great extent.

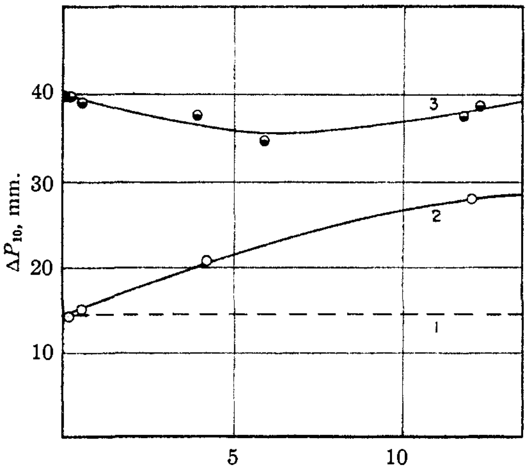

Fig. 1.—Effect of nitric oxide upon the biacetyl-promoted decomposition of acetone at 523°. Pressure increase during first ten minutes for: ●, 160 mm. acetone containing 1% biacetyl; ◒, 160 mm. acetone containing 1% biacetyl in the presence of nitric oxide; ○, 160 mm. acetone in the presence of nitric oxide. For comparison, broken line indicates ΔP_{10} for pure acetone.

The slight reduction in rate in the presence of large amounts of nitric oxide may be due either to an inhibition involving the combination of nitric oxide with radicals or to the destruction of the biacetyl by reaction with nitric oxide before the biacetyl has an opportunity to promote the decomposition of acetone. It is apparent that in the absence of biacetyl the decomposition of acetone, as well as the decomposition of acetaldehyde (see below), is accelerated by the presence of higher pressures of nitric oxide and this acceleration is probably a disturbing influence when the rate of the promoted reaction is measured in the presence of larger pressures of nitric oxide.

For Fig. 1, only experiments in the neighborhood of 523° and 160 mm. initial pressure were chosen so that corrections in the rates to these conditions were very small, amounting to a few per cent. or less. If nitric oxide acted as a satisfactory inhibitor for the biacetyl promoted reaction and had no other influence, it would be expected that the rate shown by curve 3 in Fig. 1 would at some point decrease at least to the value indicated by the broken line 1. The fact that the rate of the biacetyl promoted reaction even in presence of nitric oxide is two and one-half to three times as fast as that for pure acetone alone shows that in the presence of acetone and biacetyl the lack of appreciable inhibition by nitric oxide is not a reliable indication of the absence of a chain reaction.

Acetaldehyde.—Table II gives the data from experiments performed in order to determine the effect of nitric oxide upon the biacetyl promoted decomposition of acetaldehyde. It is evident that with acetaldehyde the promoting effect of biacetyl is greater than with acetone. Over-all pressure increases were measured at 495° for (a) acetaldehyde, (b) acetaldehyde containing 0.97% biacetyl, and (c) acetaldehyde containing 0.97% biacetyl in the presence of 4.3 mm. of nitric oxide, the initial pressures being about 194 mm. All the values of P_f/P_0, without dead space correction, are within 1% of the average value, 1.98, indicating that the over-all reaction is probably the same in the three instances, namely, decomposition into methane and carbon monoxide, and that pressure measurements can be used for comparisons of rates.

As in the case of acetone, the addition of 0.1–0.5 mm. nitric oxide, which has only little effect upon the rate of decomposition of pure acetaldehyde, does not have more than a slight inhibiting influence upon the biacetyl promoted decomposition.

As larger amounts of nitric oxide are added, the rate of the promoted decomposition is noticeably reduced. As mentioned previously, it is not known whether this decrease in the rate is due to an inhibition or to the destruction of the biacetyl by reaction with nitric oxide. However, the rate

---

[14] Rice and Walters, THIS JOURNAL, 63, 1701 (1941).

TABLE II

EFFECT OF NITRIC OXIDE UPON THE PROMOTED DECOMPOSITION OF ACETALDEHYDE

P_0 is the initial pressure of acetaldehyde plus biacetyl. ΔP_5 is given to the nearest 0.5 mm. for values below 50 mm. and for values above 50 mm. to the nearest 1 mm.

Temp., °C.	P_0, mm.	Ac_2, %	P_{NO}, mm.	ΔP_5, mm.	t_{30}, min.
496	192[a]	0.0	0.0	28.5	11.9
495	193[e]	.0	.0	29.5	11.6
496	176	.0	.0	26.0	12.0
496	198	.0	.0	31.0	11.5
495	182	.97	.0	127	1.14
496	192	.97	.0	143	0.98
495	195	.96	.0	135	1.15
495	204	.96	.099	130	1.27
495	194	.96	.47	125	1.35
495	185	.96	3.50	113	1.46
495	194	.97	3.76	116	1.56
495	191	.97	4.32	116	1.57
495	182	.96	11.9	97	1.92
495	192	.97	29.3	108	1.73
495	193	.0	0.10	29.5	11.7
495	189	.0	.46	39.5	8.2
496	190	.0	3.38	55	5.3
495	187	.0	3.57	56	5.0
495	186	.0	12.1	64	4.1
495	193	.0	29.0	83	2.9
497	201[b]	.0	0.0	33.5	10.8
497	194[c]	.0	.0	32.5	10.2
497	201[d]	1.0	.0	152	0.88
498	185[d]	1.0	.0	141	.87
497	200[d]	1.0	0.53	151	.88
497	190[c]	0.95	4.9	114	1.57
497	200[d]	1.01	11.6	99	1.66
498	205[d]	0.0	0.62	49.5	6.9
498	189[d]	.0	.57	43.5	7.3
496	189[c]	.0	4.8	53	5.5
498	189[d]	.0	13.3	64	4.2

[a] Average of four runs. [b] Average of two runs. [c] Experiments made at an earlier time in a different apparatus. [d] In experiments designated as *c* or *d* mixtures of nitric oxide and the organic compounds were introduced into the reaction vessel. In other cases nitric oxide was introduced into the reaction vessel first. [e] Since the results obtained with the two different samples of acetaldehyde were the same within the limits of experimental error, no indication of the sample used is given.

is always about three to four and one-half times the rate of decomposition of pure acetaldehyde, shown as broken line (1) in Fig. 2. If the rate ordinarily measured for acetaldehyde is actually a combination of a unimolecular reaction and a decomposition induced by an impurity in accordance with the conclusions of Morris,[7] an efficient inhibitor should reduce the rate of promoted decomposition to a point below the broken line (1) in Fig. 2.

Although at present it does not seem possible to reach a definite conclusion regarding the reason for the failure of nitric oxide to inhibit these promoted decompositions, several of the possible explanations for the lack of effectiveness of nitric oxide can be mentioned: (1) The chain reactions involved in the decomposition of certain carbonyl compounds, such as acetaldehyde or acetone, are of a type for which nitric oxide is not an efficient inhibitor. (2) The accelerating influence of nitric oxide may mask the inhibiting influence. (3) The large excess of carbonyl compound may destroy a large part of the nitric oxide or in some way render it ineffective.

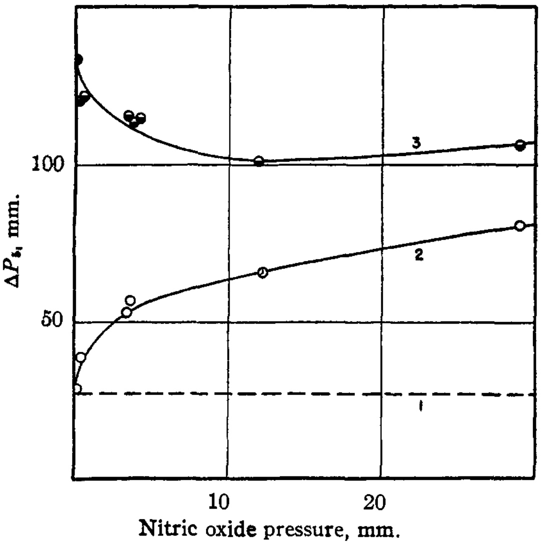

Fig. 2.—Effect of nitric oxide upon the biacetyl promoted decomposition of acetaldehyde at 495°. Pressure increase during the first five minutes for: ●, 190 mm. acetaldehyde containing 1% biacetyl; ⊖, 190 mm. acetaldehyde containing 1% biacetyl in the presence of nitric oxide; ○, 190 mm. acetaldehyde in the presence of nitric oxide. Broken line indicates ΔP_5 for acetaldehyde alone.

The results of Smith and Hinshelwood[6] indicate that (3) is probably not of importance, and they concluded that (2) is the explanation for the absence of an appreciable reduction in the rate of the acetaldehyde decomposition. Although it is evident that nitric oxide does have an accelerating influence, it is possible that another factor may also be contributing to the ineffectiveness of nitric oxide in inhibiting some decompositions.

Decomposition of Biacetyl in the Presence of Nitric Oxide.—Since biacetyl was used to promote the decomposition of acetone and acetaldehyde, a series of experiments was made to observe the effect of nitric oxide upon the decomposition of biacetyl. Experiments were carried out at 437° with initial pressures of biacetyl of approximately

TABLE III

DECOMPOSITION OF BIACETYL IN THE PRESENCE OF NITRIC OXIDE

Temp., °C.	P_{Ac_2}, mm.	P_{NO}, mm.	ΔP_{10}, mm.	$t_{12.5}$, min.
437	150	0.0	31.3	5.5
437	150	.48	31.0	5.5
437	147	5.6	33.4	5.2
437.5	149	12.5	37.8	4.4

150 mm. From the times for the pressure to increase 12.5% and from the amounts of the pressure increase during the first ten minutes, shown in Table III, it appears that nitric oxide does not inhibit the decomposition appreciably. The fact that the decomposition is inhibited to some extent by propylene[13] indicates that biacetyl is another carbonyl compound for which nitric oxide may fail to function as a reliable inhibitor. As with acetaldehyde and acetone there appears to be a positive catalysis as the nitric oxide pressure is increased.

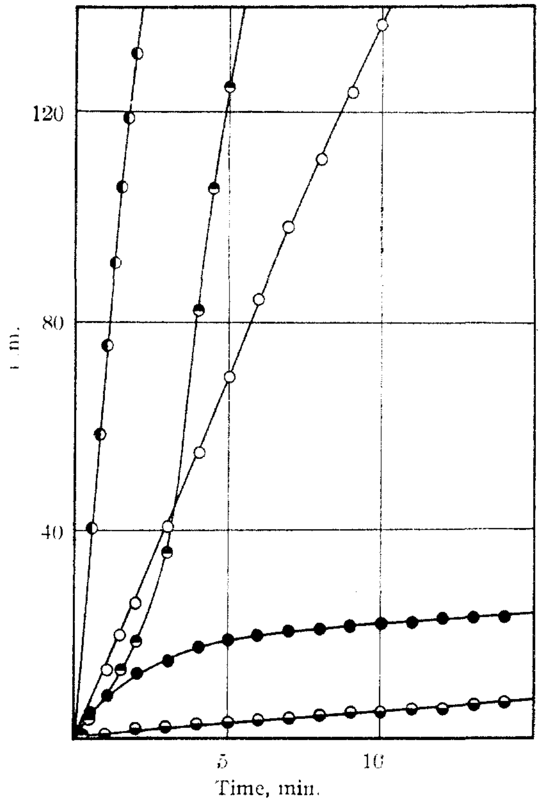

Fig. 3.—Thermal decomposition of dimethyl ether at 523°: ○, 195 mm. dimethyl ether; ◐, 190 mm. dimethyl ether containing 1% biacetyl; ◓, 210 mm. dimethyl ether containing 1% biacetyl plus 0.69 mm. nitric oxide; ●, 197 mm. dimethyl ether containing 1% biacetyl plus 5.2 mm. nitric oxide; ◒, 200 mm. dimethyl ether plus 0.68 mm. nitric oxide at 524°. 200 mm. dimethyl ether plus 5.2 mm. nitric oxide not shown, but rate is ~10% slower than with 0.68 mm.

Effect of Nitric Oxide upon the Promoted Decomposition of Dimethyl Ether.—In order to compare the effectiveness of nitric oxide in inhibiting the biacetyl promoted decomposition of a non-carbonyl compound with the results obtained with acetaldehyde and acetone, the rates of decomposition of mixtures of dimethyl ether and 1% biacetyl with and without added nitric oxide were measured at 523°. As shown by the pressure–time curves in Fig. 3, nitric oxide can inhibit to a great extent the biacetyl promoted decomposition as well as the normal decomposition. However, with the addition of 5.2 mm. of nitric oxide the inhibited promoted decomposition is still somewhat faster than the inhibited unpromoted decomposition. Although the inhibition of the biacetyl promoted decomposition requires larger amounts of nitric oxide than the inhibition of the unpromoted reaction, nevertheless nitric oxide is much more effective as an inhibitor in this case than in the promoted decompositions of acetone and acetaldehyde.

Summary

The thermal decompositions of acetone and acetaldehyde, each containing 1% biacetyl, were investigated at 523° and 495°, respectively, in the presence of 0.1 mm. to 12 mm. or more nitric oxide. The addition of nitric oxide fails to suppress the major portion of the biacetyl promoted decompositions of acetone and acetaldehyde.

It was also observed that pressures of nitric oxide from 0.5 to 12 mm. do not inhibit the thermal decomposition of biacetyl at 437°. However, the biacetyl promoted decomposition of dimethyl ether at 523° can be suppressed almost completely by the presence of nitric oxide.

ROCHESTER, NEW YORK RECEIVED NOVEMBER 13, 1944