

photometer traces and a blackening curve established from similar films developed simultaneously. In the experimental series the exposure time was varied systematically from one minute to one hour to keep the blackening between 25 and 50%. If intensities of interferences for the thinnest films are plotted against the *square* instead of the first power of the number of layers, the points between ten and thirty layers fall on a straight line. This is characteristic of an ideally imperfect diffracting medium. From a greater number of layers the intensity falls off, the upper layers shielding those below from the x-ray beam. Thus the irregularity of the first layers applied has become smoothed out and the planes approach perfection.

**Test of the Laue Particle Size Equation.**—The theoretically derived equation,  $B = b + (0.9 \lambda / D \cos \theta/2)^6$  has been used to calculate particle size in the colloidal range from the observed breadth of x-ray interferences. Until now it has been impossible to test the equation because of a lack of a comparison method. The expression is equally valid for the thickness of a built up film. The results of line breadth measurements are given in Table II. In general, agreement of observed and calculated values is good except for very thin films where the excess broadening ob-

(6)  $B$  = breadth of interference at points of half-maximum intensity;  $b$  = apparatus constant for minimum width under experimental conditions;  $\lambda$  = x-ray wave length;  $\theta$  = diffraction angle for given interference;  $D$  = size of particle, or thickness of film.

served is attributed to the previously mentioned distorted nature of the first layers applied.

TABLE II

Number of layers	Broadening			Calcd.
	Obsd.	Av.		
3	0.21	0.28	0.25	0.186
4	.27	.17	.22	.139
5	.10	.16	.13	.112
6	.15	.10	.13	.093
7	.04	.05	.05	.080
8	.06	.05	.06	.070
9	.05	.08	.06	.062
10	.05	.02	.04	.056
17	.04	.02	.03	.035
20	.02	.03	.03	.028
25	.01	.03	.02	.022
30	.02	.02	.02	.019
35	.02	.02	.02	.016

### Summary

The structures of Blodgett's composite films of stearic acid and stearates have been investigated by x-ray diffraction methods. The structure and hence the thickness have been found to be that of the constituent present in greater proportion. The  $d$  spacings agree closely with those of the crystalline material.

Intensity measurements have been made from successively increasing numbers of planes and the degree of perfection inferred therefrom.

Laue's particle size equation has been tested by the use of films of known thickness.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

## Reactions of Nickel Carbonyl with Oxides of Nitrogen<sup>1</sup>

By J. C. W. FRAZER AND WM. E. TROUT, JR.<sup>2</sup>

M. Berthelot<sup>3</sup> passed nitric oxide into nickel carbonyl and obtained a solid product. Subsequent admission of small amounts of oxygen to the reaction vessel produced another solid. Berthelot characterized both solids as complex compounds but did not give analyses. Some confusion has arisen in the literature concerning these experiments, apparently due to the mistaken translation of "bioxyde d'azote" as nitrogen per-

(1) Abstract of a dissertation submitted by Wm. E. Trout, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

(2) Present address: Department of Chemistry, Mary Baldwin College, Staunton, Virginia.

(3) Berthelot, *Compt. rend.*, **112**, 1343 (1891); *Bull. soc. chim.*, **7**, 431, 434 (1892).

oxide.<sup>4</sup> Attempts to determine the nature of the solids have not been wholly successful.<sup>5,6</sup>

This paper reports further observations concerning the reactions of nickel carbonyl with oxides of nitrogen.

### Experimental

**Nitrogen Peroxide and Nickel Carbonyl.**—Nitrogen peroxide and nickel carbonyl reacted exothermally at temperatures as low as  $-78^{\circ}$ . The reaction was carried out

(4) Muhlert, *Chem. Zentr.*, Vol. 11, 1063 (1892); Gmelin-Kraut, "Handbuch d. anorg. Chem.," Heidelberg, Carl Winter, 1909, Vol. V, p. 107; Mellor, "Comprehensive Treatise of Inorganic Chemistry," Longmans, Green and Co., London, 1928, Vol. VIII, p. 546.

(5) Mond and Wallis, *J. Chem. Soc.*, **121**, 32 (1922).

(6) Reihlen, Gruhl, Hessling and Pfrengle, *Ann.*, **482**, 161 (1930).

in four ways: (1) nitrogen peroxide was permitted to expand into the vapor of nickel carbonyl at low pressures; (2) the gaseous reactants, transported in carbon monoxide or in nitrogen, were introduced into the reaction vessel in opposing jets; (3) nitrogen peroxide diluted with nitrogen was passed over liquid nickel carbonyl at or near 0°; (4) nitrogen peroxide was admitted to solutions of nickel carbonyl in hexane. Methods 2 and 3 appeared to be most satisfactory. Special care was taken to exclude air and moisture and to purify all materials.<sup>1</sup>

The gaseous products of this reaction contained as much as 97.8% of the carbon monoxide originally combined with the nickel in the reacting nickel carbonyl. Some carbon dioxide was detected, the amount appearing to vary with the rate of admission of nitrogen peroxide, or perhaps with the temperature attained by the glass near the reaction zone.

The solid products of the reaction were obtained as a light, bulky, greenish-yellow solid which adhered to the walls of the reaction vessel. When covered with liquid nickel carbonyl, the product was apparently insoluble and unchanged. Failure to obtain x-ray patterns of the solid suggested that the material was amorphous. The solid was hygroscopic, dissolving in the water absorbed, then appearing to hydrolyze to form a green gelatinous precipitate resembling nickelous hydroxide. When treated with dilute sulfuric acid, the solid readily dissolved and oxides of nitrogen escaped. This reaction was made use of in analysis. Analyses of the solid are indicated in Table I.

TABLE I

ANALYSES OF SOLIDS RESULTING FROM REACTION OF NICKEL CARBONYL WITH NITROGEN PEROXIDE

Numbers refer to methods of preparation listed above.

Sample no.	Percentage composition		
	Ni	N	O
30 <sup>2</sup>	36.43	17.55	47.82
31 <sup>2</sup>	34.52	18.04	47.44
32 <sup>2,a</sup>	35.50	17.26	47.24
34 <sup>2</sup>	36.86	18.24	44.90
35 <sup>4</sup>	32.25	18.84	48.91
36 <sup>4</sup>	32.69	19.09	48.22
37 <sup>3</sup>	35.20	17.88	46.92

<sup>a</sup> Adsorbed oxides of nitrogen were removed from this sample before analysis.

The ratio of nitrogen as nitrate to that as nitrite was determined on Sample 37 and was found to be: N (nitrate)/N (nitrite) = 0.7469.

**Nitric Oxide and Nickel Carbonyl.**—Reaction between these compounds was markedly inhibited by carbon monoxide. In the presence of carbon monoxide under partial pressure of approximately half an atmosphere, reaction between nitric oxide and gaseous nickel carbonyl was not detected below 62°, at which temperature a bronze film appeared on the heated glass. Addition of moisture to the gases did not alter the results. When nitrogen was substituted for the carbon monoxide, reaction between nickel carbonyl and nitric oxide began immediately but was soon retarded or stopped and was far from complete after twenty-four hours. Pure nitric oxide and gaseous nickel carbonyl reacted rapidly but incompletely at room temperature, although reaction was not detected at 0°.

When nitric oxide was passed over liquid nickel carbonyl, a greater pressure of carbon monoxide was necessary to inhibit the reaction than when both reactants were in gaseous form. When pure nitric oxide was passed over liquid nickel carbonyl at 0°, twenty-five and one-half hours were required for the preparation of a maximum yield of 0.2775 g. of the solid product mentioned below.

Reaction took place as usual between nitric oxide and nickel carbonyl at room temperature in a vessel from which the light was carefully excluded.

Analysis of the gaseous products of the reaction indicated that most of the carbon monoxide initially combined with the nickel was set free. A trace of carbon dioxide was detected.

Pure nitric oxide and liquid nickel carbonyl reacted at temperatures between -11 and 0° to form a blue gelatinous solid product which became pale blue, almost white, on removal of the excess liquid nickel carbonyl. At room temperature the reaction was complicated by the formation of bronze, brown or olive-green solids. Analyses of the solid products showed large variations as shown in Table II. The pale blue solid formed at 0° was insoluble in water, but dissolved readily in dilute sulfuric acid, liberating oxides of nitrogen. Concentrated sulfuric acid reacted slowly with the solid forming a yellow suspension and liberating oxides of nitrogen and traces of carbon monoxide and carbon dioxide. When heated in hydrogen a sample of the solid slowly turned brown: at 140° reaction was rapid, leaving a dark brown solid and liberating nitric oxide. When heated in oxygen another sample of the solid rapidly turned brown at 150° and nitrogen peroxide was formed. It is interesting to note that the similar solid prepared by Mond and Wallis<sup>5</sup> decomposed violently at 90° in an inert atmosphere.

TABLE II

ANALYSES OF SOLIDS RESULTING FROM REACTION OF NITRIC OXIDE WITH NICKEL CARBONYL

9, 10 prepared at room temperature; 11-13b at 0°

Sample no.	Percentage composition		
	Ni	N	O
9	28.83	11.04	60.13
10	25.15	10.61	64.24
11	58.62	13.19	28.65
12	45.94	12.47	41.59
13a	39.19	14.35	46.46
13b	38.89	12.94	48.17

**Ammonia, Nitric Oxide and Nickel Carbonyl.**—In an attempt to stabilize the initially formed blue solid product of the reaction between nitric oxide and nickel carbonyl, ammonia at a partial pressure of 0.06 atm. was introduced into the nitric oxide and the resulting mixture was passed over liquid nickel carbonyl. Reaction occurred above -14° with the formation of a blue, gelatinous precipitate, lighter in color and more bulky than that obtained with nitric oxide alone. When the excess liquid nickel carbonyl was removed, a finely divided white solid remained, which dissolved readily in dilute sulfuric acid with the liberation of oxides of nitrogen. When exposed to the air the solid turned pink. Analyses of samples are indicated in Table III.

TABLE III

ANALYSES OF SOLIDS FORMED BY THE REACTION OF A MIXTURE OF NITRIC OXIDE AND AMMONIA WITH NICKEL CARBONYL

Sample no.	Percentage composition			
	Ni	NH <sub>3</sub>	N (additional)	O
17	27.07	34.82	14.09	24.02
22	25.06	37.23	9.89	27.82

**Ammonia and Nickel Carbonyl.**—No reaction was detected with either gaseous or liquid reagents. The solubility of nickel carbonyl in liquid ammonia at its boiling point was apparently negligible.

**Nitrogen Trioxide and Nickel Carbonyl.**—Reaction of nitrogen trioxide with nickel carbonyl took place at  $-78^{\circ}$  with the formation of a bright red solid, apparently formed only at temperatures at which the molecule  $N_2O_3$  exists. The solid slowly lost its bright red color and became reddish-yellow when warmed to  $60^{\circ}$ . We were unable to analyze the red compound, but obtained a brown solid (apparently formed by the action of nitrogen peroxide on the red solid) which had the composition: Ni, 28.95; N, 22.95; O, 48.10.

**Nitrous Oxide and Nickel Carbonyl.**—Reaction between these substances was not observed at  $0^{\circ}$ , and at room temperature the rate of reaction was negligible. A mixture of nitrous oxide and gaseous nickel carbonyl exploded when ignited with a gas flame.

**Nitric Oxide, Nickel Chloride and Grignard Reagents.**—Nitric oxide was passed through suspensions formed by addition of nickel chloride (1) to an ether and benzene solution of phenylmagnesium bromide,<sup>7</sup> and (2) to an ether solution of ethylmagnesium bromide. The green solution obtained in the latter experiment was not as intense in color as that in the former. Attempts to isolate the green substances were unsuccessful due to their high solubility and sensitivity to air. That Job and Reich,<sup>7</sup> as they suggested, prepared the compound obtained by Mond and Wallis,<sup>8</sup> is made doubtful by the facts that the green substance in solution was not decomposed by dilute sulfuric acid, and that oxides of nitrogen were not liberated by this treatment.

### Discussion of Results

The temperatures at which reaction was first detected between nickel carbonyl and oxides of nitrogen studied were roughly in the inverse order of the degree of oxidation of the nitrogen atom:  $NO_2$ ,  $-78^{\circ}$ ;  $N_2O_3$ ,  $-78^{\circ}$ ;  $NO$ ,  $-11^{\circ}$ ;  $N_2O$ , above room temperature.

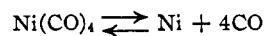
Nitrogen peroxide reacted with nickel carbonyl at  $-78^{\circ}$  and above to form a solid in which the ratio of nitrate to nitrite was in agreement with the assumption that the solid consisted of a mixture of the nickel salts of these ions (calculated for  $Ni(NO_2)_2 \cdot 0.7469Ni(NO_3)_2$ , Ni, 35.20%; found Ni, 35.71). Most of the carbon monoxide combined with the nickel was liberated as such. The products of the reaction in hexane contained more

nitrogen and oxygen than samples obtained by other methods.

Nitrogen trioxide reacted with nickel carbonyl apparently at temperatures at which the molecule  $N_2O_3$  exists. The behavior of this solid suggests the possibility that it is an addition product.

Nitric oxide reacted with nickel carbonyl above  $-11^{\circ}$  to liberate carbon monoxide and traces of carbon dioxide and to form solids which varied greatly in composition, even when prepared in consecutive vessels under the same conditions (13a and 13b, Table II). It will be noticed that the solid obtained at room temperature contained less nickel than that formed at  $0^{\circ}$  (9, 10, Table II).

The marked inhibiting effect of carbon monoxide on the reaction between nickel carbonyl and nitric oxide is somewhat similar to that reported by Dewar and Jones<sup>8</sup> on the reaction between nickel carbonyl and carbon disulfide. The phenomena in both cases are probably, as these authors suggested, explained by the influence of carbon monoxide on the stability of the nickel carbonyl in accordance with its reversible decomposition.



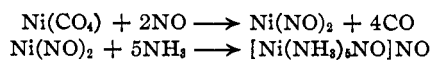
for which the equilibrium relationship is

$$K = P_{Ni} \times P_{CO}^4 / P_{Ni(CO)_4}$$

The possibility is suggested that the nitric oxide reacts not entirely with the nickel carbonyl but with its products of decomposition.

The appearance, analyses and manner of formation of the solids formed by the action of ammonia and nitric oxide on nickel carbonyl suggests the formation of complex compounds, such as  $[Ni(NH_3)_5NO]NO_2$  and  $[Ni(NH_3)_5NO]NO_3$  (Ni: calcd., 26.69 and 24.88%; found, 27.07 and 25.06%).

Ammonia did not react with nickel carbonyl at  $0^{\circ}$ , and the reaction between ammonia, nitric oxide and nickel carbonyl began at the same temperature as that between nitric oxide and nickel carbonyl. These facts suggest that the nickel carbonyl first reacts with the nitric oxide to form a product which further reacts with ammonia to form a complex compound, perhaps as indicated in the tentative equations



The  $[Ni(NH_3)_5NO]NO$  may then be oxidized to form the compounds  $[Ni(NH_3)_5NO]NO_2$  and

(7) Job and Reich, *Compt. rend.*, **177**, 1439 (1923).

(8) Dewar and Jones, *J. Chem. Soc.*, **97**, 1226 (1910).

[Ni(NH<sub>3</sub>)<sub>5</sub>NO]NO<sub>3</sub>. Briner and co-workers<sup>9</sup> have found that nitrogen peroxide is formed slowly in pure nitric oxide under pressure at ordinary temperature, and also in liquid nitric oxide under atmospheric pressure below its boiling point. The presence in the reacting gases of nitrogen peroxide so formed may explain the oxidation of the complex compound first formed, and may also explain the failure to obtain a pure solid product from the reaction of nitric oxide with nickel carbonyl.

In view of the unexplained erratic behavior of oxygen and nickel carbonyl,<sup>10</sup> the observations concerning mixtures of nitrous oxide and nickel

(9) Briner, *et al.*, *Compt. rend.*, **149**, 1372 (1909); **156**, 228 (1931); *J. chim. phys.*, **23**, 157 (1926).

(10) Hieber and Kaufmann, *Z. anorg. allgem. Chem.*, **204**, 174 (1932); Berthelot, *Bull. soc. chim.*, **7**, 434 (1892); *Compt. rend.*, **113**, 679 (1892); Lenher and Loos, *THIS JOURNAL*, **22**, 114 (1900); Blanchard and Gilliland, *ibid.*, **48**, 872 (1926).

carbonyl cannot be taken as final. Nitrous oxide may react equally unpredictably with nickel carbonyl.

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### Summary

Some observations have been reported concerning the reactions of nickel carbonyl with nitrogen peroxide, nitric oxide, nitrous oxide, ammonia and a mixture of ammonia and nitric oxide.

The suggested relationship of the results of Job and Reich<sup>7</sup> to those of Mond and Wallis<sup>5</sup> was also investigated.

BALTIMORE, MD.

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## Antioxidants and the Autoxidation of Fats. VII. Preliminary Classification of Inhibitors<sup>1</sup>

BY H. S. OLCOTT AND H. A. MATTILL

It was recently proposed<sup>2</sup> to give the name "inhibitols" to those as yet unidentified constituents of the unsaponifiable matter of various vegetables and vegetable oils which possess the capacity to delay oxidative rancidity in certain fats. This term indicates their activity as inhibitors and also the invariable occurrence of hydroxyl groups upon which their inhibiting action depends. Methods of preparation of inhibitol concentrates and some of their physical and chemical properties have been described in some detail.<sup>2</sup>

Inhibitol concentrates are effective antioxidants for animal fats and for highly purified unsaturated fatty acids and esters, but they have consistently failed to show any antioxygenic activity when added, even in relatively large amounts, to the vegetable oils from which they were obtained (Table I). The inactivity of inhibitols in vegetable oils is also implied in the experiments of Royce,<sup>3</sup> who added a crude sterol fraction of cottonseed oil to hydrogenated cottonseed oil

without observing any prolongation of the induction period, in those of Greenbank and Holm<sup>4</sup> who reported an unsuccessful attempt to isolate an antioxidant from cottonseed oil, using vegetable oils as the assay substrate, and in those of Bau-

TABLE I  
EFFECT OF INHIBITOLS ON DIFFERENT FATS

Substrate	Per cent. inhibitol concentrate added <sup>a</sup>	Induction period, days	
		With inhibitor	Control
Organoleptic method, 63°			
Cottonseed oil	0.10 C58	3.5, 4	4, 4.5
	.05 W5-10	3	3.5
	.05 W5-10	6 <sup>1</sup> / <sub>2</sub>	8
Hydrogenated cottonseed oil	.05 C44	8 <sup>1</sup> / <sub>2</sub>	8
	.02 W48	27, 31	28, 32
Lard	.03 W5-10	42, 49	41, 49
	.02 W5-10	9, 9	3, 3
	.01 W5-10	10.5, 11	4, 4
Oxygen absorption method, 75°			
		Hrs.	Hrs.
Lard <sup>b</sup>	0.02 W5-10	50	10
Oleic acid	.03 W5-10	10	4
Methyl oleate	.02 W5-10	30	4

<sup>a</sup> W indicates wheat germ oil inhibitol, C that from cottonseed oil. <sup>b</sup> See also reference 2, Tables V and VI.

(1) Presented before the Division of Agricultural and Food Chemistry at the 92nd meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

(2) H. S. Olcott and H. A. Mattill, *THIS JOURNAL*, **58**, 1627 (1936).

(3) H. D. Royce, *Oil and Soap*, **9**, 25 (1931).

(4) G. R. Greenbank and G. D. Holm, *Ind. Eng. Chem.*, **26**, 243 (1934).