be expected of the former treatment, supersonic waves might have some effect if the intensity were great enough.

The X-ray diffraction patterns shown in Fig. 3 illustrate the distortion effects. Pattern no. 1 shows the product obtained upon vacuum decomposition of $2Pb(OH)_2 \cdot 3PbO$ at 130°; pattern no. 2, the distorted PbO obtained by grinding; and pattern no. 3, the normal undistorted red PbO obtained by annealing a distorted sample at 400° for three and one-half hours. A distorted PbO can be obtained also (rather unexpectedly) by crystallization from solution. This will be discussed in the next paper.

Summary

1. Subjecting metastable, yellow orthorhombic PbO to grinding converts it to a distorted red tetragonal PbO, as is evidenced by the characteristic broadening of certain lines and the decrease in intensity of high order interferences on the X-ray diffraction pattern, as well as by the increased catalytic activity of the product.

2. A quantitative study has been made to correlate extent of grinding with degree of distortion, using the rate of decomposition of hydrogen peroxide as a measure of catalytic activity. In general, increased grinding up to ten hours produces an increase in distortion. The activity of distorted samples prepared by grinding is, in general, about the same as that produced by other methods.

3. Distortion in PbO can be relieved completely by annealing. This process is rapid at 400 and 500°, slow at 300°, and apparently almost zero at 215°. Attempts to relieve distortion by subjecting samples to liquid air temperatures and to ultrasonic vibrations were unsuccessful.

4. The fact that distortion in PbO can be removed by annealing lends further support to the theory advanced by Clark and Tyler, which states that the properties observed must be due to imperfectly crystallized areas as a result of the transition from orthorhombic to tetragonal arrangement which is still in process.

URBANA, ILLINOIS RECEIVED OCTOBER 23, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Studies on Lead Oxides.[1] V. Further Experiments on Compounds of the Type $PbO_{n(n = 1 \text{ to } 2)}$

BY GEORGE L. CLARK AND ROBERT ROWAN

I. The Addition of Oxygen to PbO and its Removal from PbO_2.—The primary purpose of this series of experiments was to determine what relation, if any, the so-called "black red lead" of LeBlanc and Eberius[2] bears to the compounds prepared by Clark, Schieltz and Quirke[3] and to further clarify the field as much as possible. This has, of course, involved the preparation of the "black red lead" and also the crystalline Pb_5O_8 and Pb_2O_3 of Clark, Schieltz and Quirke. According to LeBlanc and Eberius, the "black red lead" can be prepared by the addition of oxygen to PbO (either red or yellow) or the subtraction of oxygen from PbO_2. It was decided to make the preparation by both methods to see if they differed in so far as the X-ray pattern was concerned. Clark, Schieltz and Quirke give directions for the preparation of crystals of Pb_5O_8, Pb_2O_3 and Pb_3O_4, using a modification of the bomb method devised by Simon.[4]

Apparatus.—The apparatus used for the vacuum decomposition of PbO_2 and for the addition of oxygen to PbO at various controlled temperatures is shown in Fig. 1. It consisted of an outer cylinder of Pyrex glass eighteen inches long and three inches in outer diameter. Inside the cylinder, the heating unit consisted of a fused quartz tube eight inches long and seven-eighths inch in diameter. The quartz tube was held in the center of the outer tube by two doughnut-shaped supports of heavy asbestos board, and the alumel wire winding was insulated with asbestos paper. Two large rubber stoppers, bored for the insertion of thermocouple, vacuum system connection, and heating current wires, were flanged to make a vacuum tight seal with the ends of the outer tube. The construction of the rest of the apparatus is evident from the diagram. The chromel-alumel thermocouple was suitably standardized according to the melting points of pure zinc, lead, and tin and the boiling point of water. The heating current was controlled by means of a lampbank and stovepipe resistances. It was found that, if the room temperature remained constant, the furnace could usually be left for hours without a

---

(1) For the fourth paper of this series, see Clark and Rowan, THIS JOURNAL, **63**, 1302 (1941).

(2) LeBlanc and Eberius, *Z. physik. Chem.*, **A160**, 69 (1932).

(3) Clark, Schieltz and Quirke, THIS JOURNAL, **59**, 2305 (1937).

(4) Simon, *Z. anorg. allgem. Chem.*, **185**, 280, 300 (1930).

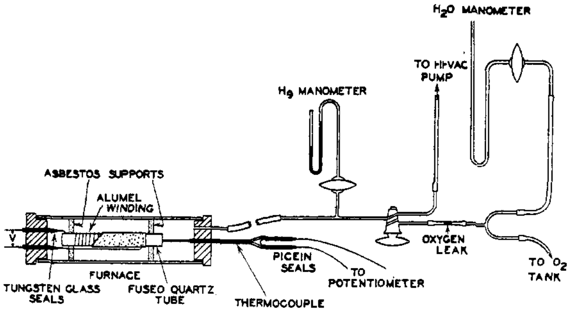


Fig. 1.—Vacuum furnace.

variation in furnace temperature of more than two or three degrees. Thermocouple voltage was measured with a Leeds and Northrup student type potentiometer, and the cold junction was always kept in ice water.

Procedure and Results.—For the decomposition of PbO_2, the sample was merely placed in a porcelain boat in the heating tube with the thermocouple junction dipped into it, the temperature adjusted to the desired value, and the vacuum pump started. If no vacuum was desired, the connection was removed and the system left open to the air. For the addition of oxygen to a sample, the system was first evacuated, after which the two-way stopcock was turned so that the oxygen could be drawn in from the oxygen tank. As soon as the pressure was equalized, the system was again evacuated. The furnace was thus "flushed" with oxygen three times. The oxygen tank valve was adjusted so that there was a constant slight flow of oxygen through the "leak," a small slit in a rubber tube, and so that the pressure remained slightly above atmospheric, as shown on the water manometer. Once adjusted, the oxygen pressure remained constant without any further attention except when the treatment was for more than a day.

The procedure for active oxygen determinations performed on almost all samples was the Diehl-Topf method recommended by Mrgudich and Clark,[5] who made a comprehensive study as to the most reliable of the existing methods. This procedure was found to give excellent checks for the same sample. The method consists in a solution of the sample in a mixture of sodium acetate, acetic acid, and potassium iodide and titration of the liberated iodine with standard thiosulfate.

Results and Conclusions.—A large number of preparations were made, the most significant of which are described in Table I.

The conclusions which can be drawn can be tabulated as follows.

(a) First, and most important, the material which LeBlanc and Eberius called "black red lead" and to which they assigned the formula Pb_3O_4 is in reality a mixture of Pb_5O_8, first prepared in the macro-crystalline form by Clark, Schieltz and Quirke, and a new, previously undistinguished phase, which we shall call PbO_x. This new phase has been obtained only by adding oxygen to the PbO lattice and never by subtract-

TABLE I

Sample	Preparation	Hr.	Value for n if formula is written PbO_n	X-Ray pattern
1	PbO_2 (Fresh)		1.961	PbO_2
2	PbO_2, 200°, Vac.	3		PbO_2 (unchanged)
3	200°	12		PbO_2 (unchanged)
4	300°	3		PbO_2 (unchanged)
5	300°	12	1.930	PbO_2 (unchanged)
6	400°	1	1.637	Pb_5O_8 + Sl. PbO_2
7		1.5	1.517	Pb_5O_8
8		2.5	1.411	Pb_5O_8
9		4.5	1.299	Some PbO(R) + Pb_5O_8 + Sl. Pb_3O_4
10		12	1.163	Mostly PbO(R) + Some Pb_3O_4
11	500°	0.75		Equal PbO(R) and Pb_3O_4
12	500°	3		Mostly PbO(R) and some Pb_3O_4
13	350°, Air	3	1.750	Mostly PbO_2 + Pb_5O_8
14	350°	18	1.563	Pb_5O_8
15	385°	5.5	1.519	Pb_5O_8
16	385°	24	1.446	Pb_5O_8 – PbO(R)
17	500°	1		Equal PbO(R) and Pb_3O_4
18		2		Pb_3O_4 + trace of PbO(R)
19	Pb_3O_4	3		PbO(Y)
20	PbO(R), 350°, O_2	3	1.149	PbO(R) + Pb_5O_8 (trace)
21		12	1.436	Equal PbO_x and Pb_5O_8
22		24	1.447	Equal PbO_x and Pb_5O_8
23		36	1.454	Some PbO_x and Pb_5O_8
24		48	1.462	Some PbO_x and lot Pb_5O_8
25	385°	12	1.374	PbO_x + trace Pb_5O_8
26	400	2	1.343	Pb_3O_4 only
27	425°	1.5	1.358	Equal Pb_3O_4 and PbO_x
28	PbO(Y), 350°	12	1.074	PbO(Y)
29	PbO(Y), 350°, O_2	24	1.101	PbO(Y) + V. Sl. Pb_5O_8
30	PbO(Y), 400°	2	1.078	PbO(Y) + Sl. Pb_3O_4
31	PbO(Y), 500°	8	1.272	Pb_3O_4 + Sl. PbO (Y)
32A[a]	PbO(R), 350°	7.5	1.369	PbO_x + cons. Pb_5O_8
32B[a]	PbO(Dist.), 350°	7.5	1.485	Pure Pb_5O_8 (Dist.)
33A[a]	PbO(R), 350°	9	1.376	Equal PbO_x and Pb_5O_8 (Dist.)
33B[a]	PbO(Dist.), 350°	9	1.487	Pb_5O_8 and trace PbO_x
34A[a]	PbO(R), 350°	24	1.416	PbO_x + Sl. Pb_5O_8
34B[a]	PbO(Dist.), 350°	24	1.440	Pb_5O_8 pure
35	PbO(Dist.), 385°	3	1.409	Mostly Pb_5O_8. Some PbO_x
36A[a]	PbO(R), 385°	9	1.372	Pb_5O_8 pure
36B[a]	PbO(Dist.), 385°	9	1.486	PbO_x + Sl. trace Pb_5O_8
37	$PbCO_3$, 215°, Vac.	24		PbO (Dist.)
38	$PbCO_3$, 215°, Vac.	72	1.002	PbO (Dist.)

[a] Identical, simultaneous treatment for samples marked A and B. Dist. = Distorted; Sl. = Slight; cons. = considerable; R = red, tetragonal; Y = yellow, orthorhombic.

---

(5) Mrgudich and Clark, *Ind. Eng. Chem., Anal. Ed.*, **9**, 256 (1937).

ing oxygen from the PbO_2 lattice, though Pb_5O_8 can be prepared by either method. As in the case of Pb_5O_8 lattice, the PbO_x lattice seems to be able to take on or give up oxygen without breaking down. For this reason, and because it has not been obtained in an absolutely pure form, it is not possible to assign a formula to it at present. However, it is not unreasonable to believe that it may be a missing link, Pb_5O_7, or Pb_3O_5, in the series of mixed oxide compounds: $2PbO{\cdot}PbO_2$; $3PbO{\cdot}2PbO_2$; $PbO{\cdot}PbO_2$; $2PbO{\cdot}3PbO_2$; $PbO{\cdot}2PbO_2$.

(b) Distorted PbO reacts with oxygen much faster than normal PbO, as can be seen from an examination of the pairs of samples designated A and B. In each case, samples of normal and distorted PbO were placed in the same clay boat in the furnace and given simultaneous treatment. For each pair of samples, the one starting with distorted PbO always showed the higher active oxygen content. This greater velocity of absorption was also evident from the color of the sample during the preparation, as the distorted PbO turned to a brown color much more rapidly. This difference is not so great for long treatment. This fits in with the observation of Sapgir, who found that preheated PbO was oxidized more slowly than unheated PbO. Probably any distortion in the PbO was removed by the heat treatment.

(c) The product obtained from the absorption of oxygen by distorted PbO was usually pure Pb_5O_8, while the product starting with normal PbO was usually a mixture of Pb_5O_8 and PbO_x, with the tendency toward the formation of PbO_x. This tendency increased as the temperature was raised to 385°, a point nearer to the transition temperature for $Pb_5O_8 \xrightarrow{390°} Pb_3O_4$, so that in the case of distorted PbO, pure Pb_5O_8 was formed and in the case of normal PbO, almost pure PbO_x was formed.

(d) Red PbO absorbs oxygen faster than yellow PbO. This is a contradiction of the work of Le Blanc and Eberius, who state that essentially the same results were obtained for both lead monoxides. A comparison of sample no. 29 and no. 22 shows only a slight absorption by yellow PbO with only a trace of the Pb_5O_8 lattice, and complete conversion for red PbO.

(e) The PbO_x lattice gives a rather complicated X-ray pattern, and it is not possible to determine its crystal system at present. It appears, however, to be monoclinic or triclinic. The interplanar spacings are listed in Table II.

TABLE II

INTERPLANAR SPACINGS AND INTENSITIES FOR X-RAY PATTERN OF PbO_x

Line no.	*d*	Estimated[a] intensity	Line no.	*d*	Estimated intensity
1	3.018	S	12	1.660	M
2	2.918	WW	13	1.636	S
3	2.850	M	14	1.616	W
4	2.558	F	15	1.513	W
5	2.383	W	16	1.312	WW
6	2.127	WW	17	1.286	F
7	1.964	S	18	1.191	WW
8	1.783	M	19	1.129	WW
9	1.767	WW	20	1.090	F
10	1.704	F	21	1.061	F
11	1.678	WW	22	0.930	F

[a] SS = very strong; S = strong; M = medium; W = weak; WW = very weak; F = faint.

(f) The fact that distorted PbO reacts completely and homogeneously with oxygen to give Pb_5O_8, a reaction definitely different from that of normal red PbO, strongly indicates that distortion in PbO is not solely a surface phenomenon, as Clark and Tyler postulated. It could still, however, be a disoriented lattice with perhaps atoms missing at random throughout.

(g) It is suggested that the greater absorptive power of distorted PbO for oxygen be used as a criterion for the activity of the sample rather than the catalytic decomposition of hydrogen peroxide.

(h) There is some indication (samples no. 22, 23, 24) that PbO_x is converted into Pb_5O_8 on long heating in oxygen.

(i) Most of the oxygen absorption of PbO took place at the beginning of the heating period. This was especially true of distorted PbO.

(j) A considerable distortion effect has been noted in Pb_5O_8. In the normal case, there was a certain line doubling which was not present in certain samples prepared from distorted PbO.

(k) Pb_3O_4 which is prepared in such a way that Pb_5O_8 is an intermediate product (samples no. 9, 10, 11, 12, 18, 31) shows a very decided distortion similar to that found in PbO, which is characterized by a blurring of some X-ray lines while others remain sharp and a general decrease in intensity of high-order interferences. Distorted Pb_3O_4 has not been reported in the literature.

(l) Distortion in PbO is not an active oxygen phenomenon. This is proved by the active oxygen determination on sample no. 38, showing that there was certainly not enough excess oxygen in the lattice to account for its distorted character.

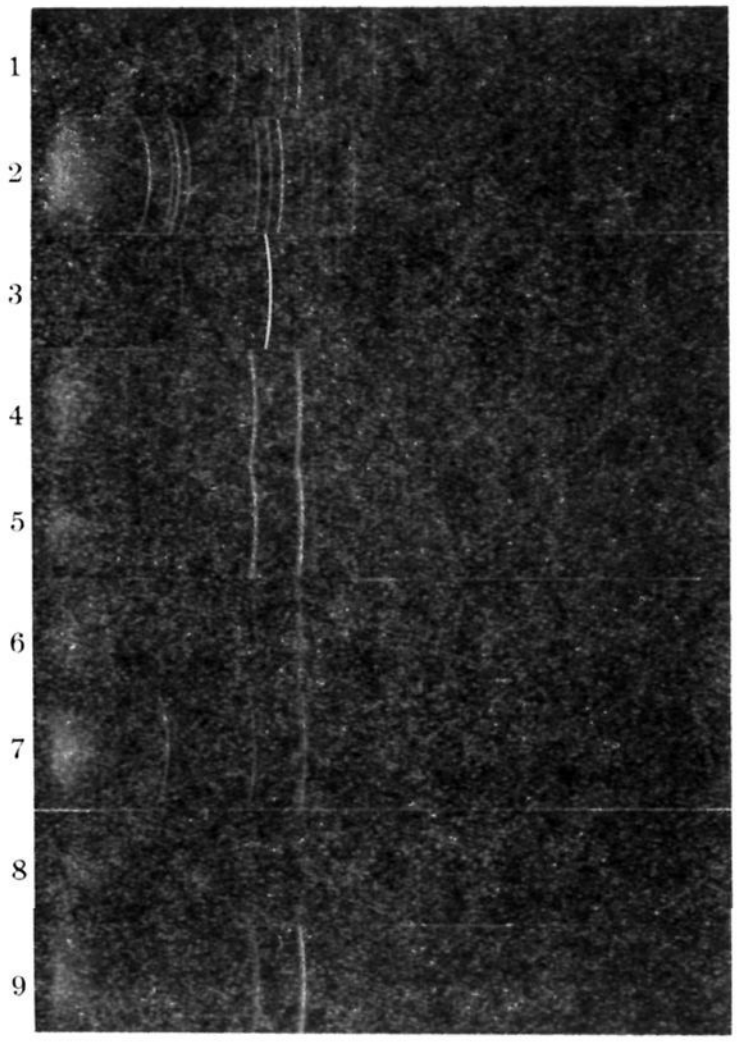


Fig. 2.—Diffraction patterns of
Pb_2O_3, Pb_3O_4, PbO_2, Pb_5O_8 and PbO_x.
1 2 3 4–6 7–9

Many of the above conclusions may be clarified by examination of the X-ray patterns in Fig. 2, respectively, for:

1. Pb_2O_3—obtained from a bomb
2. Pb_3O_4
3. PbO_2
4. Pb_5O_8—made from PbO_2
5. Pb_5O_8—obtained from a bomb
6. Pb_5O_8—obtained by addition of O_2 to distorted PbO at 385°
7. PbO_x—(− slight Pb_5O_8)—obtained by addition of O_2 to normal PbO
8. PbO_x—best sample obtained. Normal PbO in O_2 at 385°
9. PbO_x—Pb_5O_8 mixture such as obtained by LeBlanc and Eberius. Prepared by treatment of PbO with O_2 at 350°, 36 hours

II. Progress in the Determination of the Structure of Pb_5O_8.—Clark, Schieltz and Quirke reported, on the basis of microscopic examination, that Pb_5O_8 belonged to the tetragonal system with the *a*, *b* dimensions slightly different from *c*. It was hoped that a unit cell size determination could be made from a powder pattern, since the crystal was so nearly cubic.

Table III gives the measured interplanar spacings, estimated intensities, and the tentatively assigned indices. On this basis, the unit cell dimensions are: $a, b = 5.508$ Å.; $c = 5.460$ Å.

TABLE III

INTERPLANAR SPACINGS, INTENSITIES, AND PROBABLE *hkl* VALUES FOR X-RAY PATTERN OF Pb_5O_8

Line no.	*d*	Estimated intensity	Probable *hkl*
1	3.143	S	111
2	2.730	S	200
3	1.940	SS	220
4	1.877	S	202
5	1.656	SS	311
6	1.640	S	113
7	1.590	W	222
8	1.572	M	
9	1.377	WW	400
10	1.367	F	004
11	1.258	M	331
12	1.248	W	313
13	1.230	M	420
14	1.216	W	402
15	1.124	W	422
16	1.113	W	224
17	1.060	WW	511
18	1.047	WW	115
19	0.830	WW	531
20	0.916	F	513

The proposed set of indices fits so well on the reciprocal lattice graph,[6] with the single exception of no. 8 (probably an impurity or superlattice effect), that the unit cell dimensions must be either those listed or some multiple of them.

Using the density value 9.514, determined by Clark, Schieltz and Quirke, and the unit cell dimensions listed, the calculation of the number of molecules per unit cell gives a value of approximately 1.

In an attempt to prepare crystals of Pb_5O_8 large enough for Laue and rotation patterns, the bomb method of Clark, Schieltz and Quirke was used. The crystals so obtained were larger than any obtained by Clark, Schieltz and Quirke. They were carefully mounted on small strips of cellophane with rubber cement so that manipulation was possible, and several Laue patterns were made. The method was unsuccessful, however, for the apparently perfect crystals proved to be oriented small crystal agglomerates, so that the Laue spots were too blurred for measurement. Further trials of this kind might yield results.

---

(6) Clark, "Applied X-Rays," 3rd ed., New York, 1940, p. 301.

One interesting and unexpected discovery was made. The liquid contained in the bomb after heating was allowed to stand in a crystallizing dish. The resulting crystals were dark red, almost black, irregularly shaped bodies. When crushed and subjected to X-ray examination, they gave the pattern of very distorted PbO. This is believed to be the first time distorted PbO has been prepared by a wet method.

III. Effect of Sulfamic Acid on Active Oxygen Content of PbO_2.—PbO_2 having the theoretical oxygen content has rarely been obtained, most samples having a formula, on the basis of active oxygen analyses, of $PbO_{1.94}$ to $PbO_{1.98}$. The tetragonal crystal structure actually is maintained down to $PbO_{1.66}$.[2] Thus, it is evident that the problem of the preparation of PbO_2 having the theoretical formula is of considerable interest. On the theory that the deficiency in oxidizing power is due to the presence of plumbous ions in the lattice, an attempt was made to dissolve such ions from the lattice by extraction with sulfamic acid, whose plumbous salt is very soluble. The active oxygen content decreased, however, rather than increased, as can be seen from the representative data:

	Active oxygen
PbO_2—starting material	95.1%
After 24 hrs. shaking, satd. sulfamic acid	93.4%
After 48 hrs. shaking, satd. sulfamic acid	88.6%

Active oxygen determinations were made by the Diehl–Topf method, described in a previous section.

The X-ray patterns of the extracted samples showed the development of the Pb_3O_4 lattice, the amount of Pb_3O_4 increasing with time of extraction.

IV. The Preparation and X-Ray Study of Black Lead Monoxide.—Black PbO has been prepared and studied by several investigators, the most recent work having been done by Garrett, Vellenga, and Fontana.[7] No X-ray examination has been made, however. Since the final answer as to whether or not a new crystalline phase exists lies in the X-ray pattern, this material was prepared and X-ray patterns were made.

The method of preparation was that described by Garrett and co-workers, which consisted in very slowly cooling a saturated solution of white, hydrated lead oxide in 6 *N* sodium hydroxide from about 80°. It was found that very slow cooling indeed (over a period of twenty-four hours) was required. After several trials, however, a very good crop of graphite-like crystals was obtained.

The X-ray patterns of these crystals showed the presence of nothing except yellow PbO. Thus, the black color must be due to a surface effect. Appleby[8] claims that the black color is a thin film of lead produced by the action of heat or light. The X-ray results are in accord with this theory, since the lead may well be present in such a small relative quantity, and so finely divided, that it cannot be detected by the X-ray method.

Summary

1. The lead oxide phase first described by Le Blanc and Eberius, to which they assigned the formula Pb_3O_4 and called "black red lead," has been prepared and studied. Macro-crystals of Pb_5O_8 and Pb_2O_3 have been prepared by the bomb method of Clark, Schieltz and Quirke, who first identified these phases. A comparison has been made between the "black red lead" and Pb_5O_8 and Pb_2O_3.

2. The "black red lead" of LeBlanc and Eberius is in reality a mixture of Pb_5O_8 and a new, previously undistinguished phase, which we shall call PbO_x. Pb_2O_3 does not occur in this system.

3. Interplanar spacings have been tabulated for the new phase, although a crystal system or unit cell determination is not possible without supplementary data. The appearance of the X-ray pattern leads to the suggestion that it may be monoclinic or triclinic, probably near orthorhombic.

4. The product obtained from the absorption of oxygen near 390° (the transition temperature for $Pb_5O_8 \rightarrow Pb_3O_4$) by normal PbO was almost pure PbO_x. With distorted PbO, the product was pure Pb_5O_8.

5. Distorted PbO absorbs oxygen much faster than normal PbO. The rate of oxygen absorption is suggested as a measure of distortion in place of the rather unreliable decomposition of H_2O_2 method.

6. A tentative unit cell size determination has been made on Pb_5O_8 from the analysis of a powder pattern. According to this, Pb_5O_8 is tetragonal, $a = 5.508$, $c = 5.460$ Å., and there is one molecule per unit cell. An unsuccessful attempt was made to prepare crystals of Pb_5O_8 large enough for

---

[7] Garrett, Vellenga and Fontana, THIS JOURNAL, **61**, 367 (1939).

[8] Appleby, *J. Chem. Soc.*, 2821 (1931).

Laue and rotation patterns. An improvement in the reported procedure, however, resulted in the production of better crystals than had been obtained previously.

7. In an attempt to prepare PbO_2 having the theoretical oxygen content, the effect of sulfamic acid on PbO_2 was studied. It was found that sulfamic acid extraction lowers the active oxygen content in proportion to the length of treatment. X-Ray examination showed the presence of Pb_3O_4 in the extracted samples.

8. Black PbO, which has been reported by several investigators, was prepared and subjected to X-ray examination. The black color is apparently a surface phenomenon, as claimed by Appleby, since no lattice could be detected, except that of the expected yellow PbO.

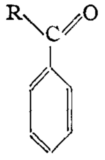
URBANA, ILLINOIS RECEIVED OCTOBER 23, 1940

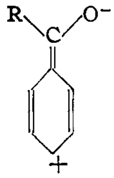
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

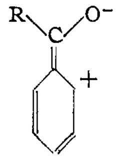
The Steric Inhibition of Resonance in Aromatic Carbonyl Compounds

BY RICHARD G. KADESCH AND SOL W. WELLER[*]

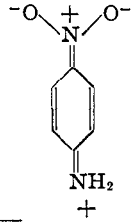
According to resonance theory aromatic carbonyl compounds are best represented as combinations of the classical structure I and quinonoid structures such as II and III.

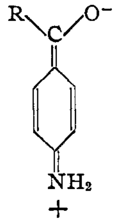

I

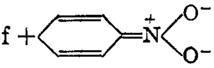

II

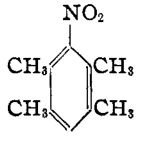

III

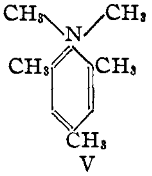
In addition to accounting for the meta-directing properties of such groups, it is the contributions of such quinonoid structures to the normal state of the molecule which lead to larger dipole moments for aromatic compounds of this type than for the corresponding aliphatic molecules. A further manifestation of the contributions from quinonoid structures of the above type is the abnormally high dipole moment of molecules which contain an electron-donating group para to the original electron-accepting group; examples of this are *p*-nitraniline and *p*-aminoacetophenone.[1] These abnormally high moments have been explained[2] as being due to contributions of the following type to the normal state of the molecule





If, for any reason, the contributions of structures II and III should be made less important, the dipole moment of the molecule should be lessened and should approach the value for the corresponding aliphatic type. It was first pointed out by Birtles and Hampson[3] that one should expect to accomplish this with the nitro group by the introduction of methyl groups ortho to it. This should reduce the contribution of  because of the steric hindrance to the oxygen atoms which must become coplanar with the benzene ring in such a structure. Birtles and Hampson confirmed this prediction when they found that the dipole moment of nitrodurene (IV) was only 3.39


IV


V

D as compared with that of nitrobenzene (3.95 *D*) whereas aliphatic nitro compounds have moments of about 3.1 *D*. Subsequently Ingham and Hampson[4] found that the dimethylamino group in dimethylmesidine (V) is also hindered from attaining the coplanar configuration of the quinonoid structure. It is seen that the use of compounds of the type of IV and V permits a direct comparison of the moment with that of the corresponding non-methylated compound since the resultant moment of the ring methyl groups is zero in either case. The inhibition of resonance of the nitro[5] and dimethylamino[6] groups by ortho

---

[*] Present address: Chemistry Department, New York University.

[1] Sidgwick, *et al.*, "Table of Dipole Moments," *Trans. Faraday Soc.*, **30**, 904 (1934).

[2] Marsden and Sutton, *J. Chem. Soc.*, 599 (1936); Bergmann and Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936).

[3] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937).

[4] Ingham and Hampson, *ibid.*, 981 (1939).

[5] Spitzer and Wheland, THIS JOURNAL, **62**, 2995 (1940).

[6] Brown, Widiger and Letang, *ibid.*, **61**, 2597 (1939).