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Ozonization of Triphenylmethane Dyes

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The reaction of Malachite Green (MG, **1a**), a model compound of triphenylmethane dye, with ozone proceeded *via* two paths. The first path involved an ozone attack at the dimethylamino moiety to give a *N*-formylmethylamino derivative **4a**. The second path produced 4-(dimethylamino)benzophenone (**2a**) and *p*-(dimethylamino)phenol (**6**). Other ozonized products, **3a** and **5a** were also detected. The following is a discussion of the ozonization mechanism.

The reactions of dyes with ozone have been studied from the point of dye-wastewater treatment. Currently, such reactions are being looked at in terms of the decrease in the chemical oxygen demand (COD) and decolorization.[1] However, the ozonization mechanism has scarcely been touched. In this respect, the ozonization reactions of pyrazolone,[2] azo,[3–6] indigoid,[7] and diphenylmethane[8] dyes have been reported.

Reactions involving triphenylmethane dyes have been discussed regarding photo-fading. The photoreaction of MG in water was reported to give 4-(dimethylamino)benzophenone, the carbinol base of MG, and *p*-(dimethylamino)phenol.[9] The photoreactions of Crystal Violet (CV) have been reported to give *p*-(dimethylamino)phenol, 4,4′-bis(dimethylamino)benzophenone, the leuco and demethylated derivatives of CV, *etc.*[10–12]

The ozonization reaction of MG, a model compound of the triphenylmethane dye, is discussed.

Experimental

General. Ozone was generated by a Nihon ozon 0-1-2 type ozonizor. IR, NMR, and mass spectra were recorded on a Hitachi EPI-S2 spectrometer, a Hitachi R-24 spectrometer, and a Hitachi M-52 spectrometer, respectively. Melting points were measured with a Yanagimoto micro-melting-point apparatus. Gas chromatography was performed using Shimadzu 3AH and 4C-PF gas chromatographs. Purity of the materials used was confirmed by gas chromatography.

Materials. The materials which were used are shown in Figure 1. **1a** (MG, Nakarai Chemicals, Ltd.) was recrystallized from benzene–ethanol; ^{1}H (CDCl$_3$) δ=3.35 (12H, s) and 6.8—7.9 (13H, m). **1b** was synthesized as described in the literature;[13] ^{1}H NMR (CDCl$_3$), δ=2.88 (12H, s), 3.53 (3H, s), and 6.5—7.1 (12H, m). **1c** was also synthesized as described in the literature;[13] ^{1}H NMR (CDCl$_3$) δ=3.00 (12H, s) and 7.0—8.0 (12H, m). **1d** (CV, Nakarai Chemicals, Ltd.) was recrystallized from water; ^{1}H NMR (CDCl$_3$) δ=3.28 (18H, s) and 6.9—7.4 (12H, dd). Dimethylaminobenzophenones **2a—c** were synthesized as described in the literature,[14] and recrystallized from ethanol. 4-(Dimethylamino)benzophenone (**2a**); mp 87.5—89.0 °C (lit 89.5—90.5 °C).[14] 4-Dimethylamino-4′-methoxybenzophenone (**2b**); mp 131.4 °C (lit 133 °C).[15] 3-Nitro-4′-(dimethylamino)benzophenone (**2c**); mp 173.6 °C (lit 173 °C).[15] 4,4′-Bis(dimethylamino)benzophenone (**2d**) was synthesized by the oxidation of Auramine O;[16] mp; 171.0—172.3 °C (lit 172—174 °C).[17] *N*-Formylmethylaminobenzophenones **3a—d** were synthesized by the oxidation of the corresponding *p*-(dimethylamino)benzophenones **2a—d** with Collins reagent[18] and purified by column chromatography (silica gel, acetone). 4-(*N*-Formylmethylamino)benzophenone (**3a**); mp 188.5 °C; ^{1}H NMR (CDCl$_3$) δ=3.42 (3H, s), 7.3—8.0 (9H, m), and 8.75 (1H, s); MS (20 eV) *m/z* (rel intensity) 239 (M$^+$; 26), 238 (1), 162 (26), 134 (24), 105 (44), and 77 (100); IR (KBr disk) 1600 cm^{-1} (C=O). 4-(*N*-Formylmethylamino)-4′-methoxybenzophenone (**3b**); mp 132.8 °C; ^{1}H NMR (CDCl$_3$) δ=3.35 (3H, s), 3.38 (3H, s), 6.9—7.9 (8H, m), and 8.63 (1H, s); MS (20 eV) *m/z* (rel intensity) 269 (M$^+$; 37), 268 (1), 162 (20), 135 (100), and 107 (17); IR (KBr disk) 1600 cm^{-1} (C=O). 3-Nitro-4′-(*N*-formylmethylamino)benzophenone (**3c**); mp 145.4 °C; ^{1}H NMR (CDCl$_3$) δ=3.38 (3H, s), 7.2—8.6 (8H, m), and 8.73 (1H, s); MS (20 eV) *m/z* (rel intensity) 284 (M$^+$; 30), 162 (26), 150 (9), 134 (100), and 122 (4); IR (KBr disk) 1605 (C=O), 1530, and 1320 cm^{-1} (NO$_2$). 4-(Dimethylamino)-4′-(*N*-formylmethylamino)benzophenone (**3d**); mp 170.1 °C; ^{1}H MNR (CDCl$_3$) δ=3.08 (3H, s), 3.40 (6H, s), 7.3—7.9 (8H, m), and 8.63 (1H, s); MS (20 eV) *m/z* (rel intensity) 282 (M$^+$; 63), 281 (13), 267 (54), 162 (4), 148 (100), 134 (33), and 120 (8); IR (KBr disk) 1600 cm^{-1}

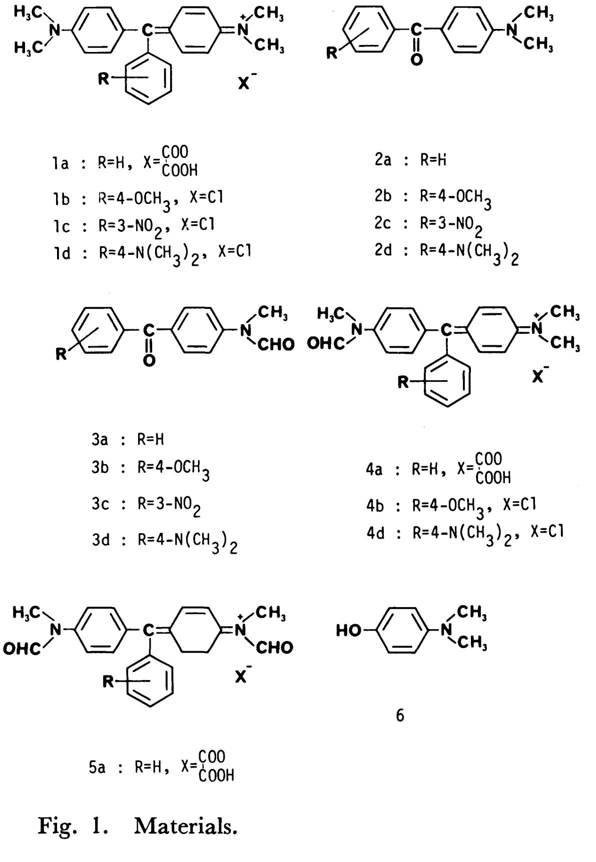


Fig. 1. Materials.

(C=O). **4a** was synthesized by the oxidation of **1a** with Collins reagent and purified by column chromatography (silica gel, acetone); ^{1}H NMR (CDCl$_3$) δ=2.90 (3H, s), 3.25 (6H, s), 7.0—7.6 (13H, m), and 8.42 (1H, s); MS (20 eV) *m/z* (rel intensity) 344 (100), 343 (10), 267 (60), and 210 (50). **4b** was isolated by the ozonization of **1b** and purified by column chromatography (silica gel, methanol : acetone=1 : 3); ^{1}H NMR (CDCl$_3$) δ=2.93 (6H, s), 3.38 (3H, s), 3.78 (3H, s), 6.7—7.4 (12H, m), and 8.40 (1H, s); MS (20 eV) *m/z* (rel intensity) 374 (100), 373 (17), 267 (15), and 240 (46). **4d** was synthesized by the oxidation of **1d** with Collins reagent; ^{1}H NMR (CDCl$_3$) δ=2.98 (12H, s), 3.05 (3H, s), 6.6—7.1 (12H, m), and 8.41 (1H, s); MS (20 eV) *m/z* (rel intensity) 387 (35), 386 (15), 267 (50), 253 (100), 134 (25), and 120 (60). **5a** was synthesized by a further oxidation of **1a** with Collins reagent; ^{1}H NMR (CDCl$_3$) δ=3.20 (6H, s), 7.0—7.5 (13H, m), and 8.30 (2H, s); MS (20 eV) *m/z* (rel intensity) 358 (3), 357 (10), 224 (6), 134 (22), and 77 (100). *p*-(Dimethylamino)phenol (**6**) was synthesized as described in the literature;[9] mp 74.1 °C (lit 74—76 °C).[19] The mass spectra of **4a**, **4b**, **4d**, and **5a** were recorded as the leuco derivatives.

Ozonization. The method of ozonization was the same as that described in a previous paper.[8] Ozonization was carried out with an ozone-oxygen mixture (ozone: 9.0 mg min^{-1}, oxygen: 200 cm^3 min^{-1}) on 0.136 mmol of substrate in 10 ml of solvent. Excess ozone was determined by iodometric titration. The ozonization products were analyzed using gas chromatography and identified by comparing their mass spectra with those of authentic samples. Yields were determined by comparisons with standard solutions of known compounds by GLC using 2% Silicone OV-1, 2% FFAP, and Chromosorb 101 columns.

Results and Discussion

When MG (**1a**) was ozonized, 4-(dimethylamino)benzophenone (**2a**), 4-(*N*-formylmethylamino)benzophenone (**3a**), *N*-formylmethylamino derivative **4a**, *N,N'*-diformylmethylamino derivative **5a**, and *p*-(dimethylamino)phenol (**6**) were detected. The result is shown in Table 1. In each case, a trace amount of **5a** was detected. Since no significant difference between the distribution of the products found in methanol and that found in dichloromethane was observed (runs 1 and 2), the possibility that a reaction of **1a** with the peroxides formed through the ozonization of methanol yielded the products was excluded. The reaction of **1a** with ozone proceeds *via* two paths. The first path produces **4a** *via* an ozone attack at the dimethylamino moiety of **1a**. The second path produces **2a** and **6** *via* an ozone attack at the carbon adjacent to the triphenylmethyl carbon of **1a**. **2a**, and **4a** are further ozonized to give **3a**, **5a**, and **6**. The ratio of the ozone attack on each position was calculated from the yields of **4a** and **2a**. The results are also shown in Table 1. The ratio N/C decreased with increasing temperature (runs 1, 3, and 4), since the reactivity of **2a** with ozone increases with decreasing temperature. Yields of the products decreased as the ratio of water in methanol increased (runs 4, 5, 6, 7, and 8). Ozone decomposes easily in water to give an hydroxyl radical which is a strong oxidizing agent.[20] The products detected by the ozonization of **1a**, however, were not obtained in the reaction of **1a** with Fenton's reagent, which generates a hydroxyl radical. The ratio of ozone(consumed)/**1a**(reacted) increased as the ratio of water in methanol became greater (runs 4, 5, 6, 7, and 8). From these results, it was found that the added water played only a role involving the acceleration of the decomposition of ozone to give a hydroxyl radical. Then, yields of the ozonization products decreased.

The substituent effect on the ozonization of **1a** is shown in Table 2. When **1c** was ozonized, ketone **2c** and *p*-(dimethylamino)phenol (**6**) were predominantly produced. On the other hand, ozonization of **1d** preferentially afforded *N*-formylmethylamino derivative **4d**. When **1a** and **1b** were ozonized, the ketones, the *N*-formylmethylamino derivative, and *p*-(dimethylamino)phenol were detected, respectively. The ratio N/C changed drastically and was in the order **1c**<**1a**<**1b**<**1d**, which consists with that of electron-donative ability of the substituent. This result suggests that an electrophilic ozone attack takes place on the dimethylamino nitrogen.

The probable ozonization mechanism of the dimethylamino moiety of **1a** is proposed in Scheme 1, by reference to the ozonization mechanism of aromatic

TABLE 1. OZONIZATION OF **1a**[a)]

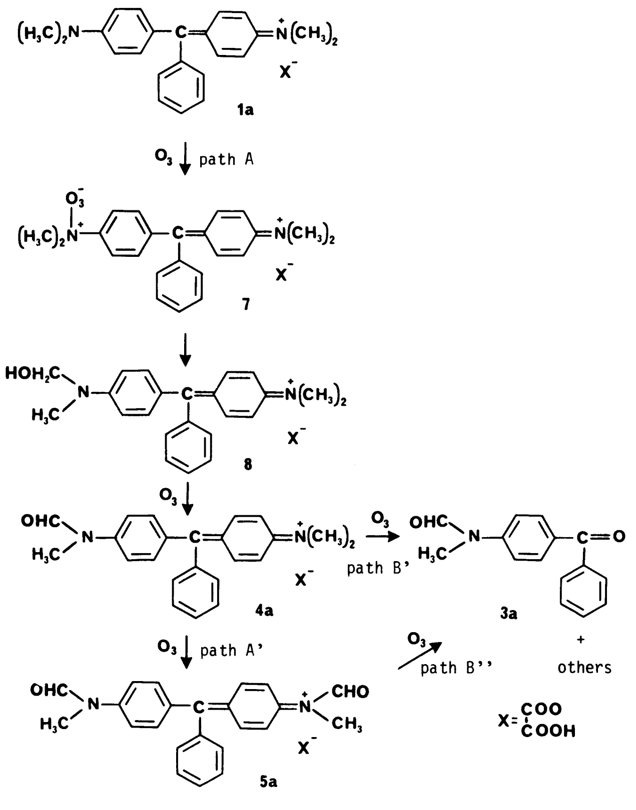
Run	Temp / °C	Solvent	Ozone consumed / 10^{-4} mol	**1a** reacted / 10^{-4} mol	Yield[b)]/% **2a**	**3a**	**4a**	**6**	Ozone (consumed) / **1a** (reacted)	N/C[c)] attack
1	−78	CH_3OH	0.40	0.34	7	1	47	10	1.2	6.7
2	−78	CH_2Cl_2	0.58	0.36	5	2	41	8	1.6	8.2
3	−20	CH_3OH	0.40	0.32	9	1	54	11	1.3	6.0
4	0	CH_3OH	0.34	0.31	18	trace	45	18	1.1	2.5
5	0	$CH_3OH : H_2O = 3 : 1$	1.14	0.41	8	3	19	12	2.8	2.4
6	0	$CH_3OH : H_2O = 1 : 1$	2.07	0.52	3	trace	8	5	4.0	2.7
7	0	$CH_3OH : H_2O = 1 : 3$	2.78	0.59	3	trace	5	4	4.7	1.7
8	0	H_2O	3.89	0.73	1	trace	0	3	5.3	0

a) Ozonization was carried out with an ozone-oxygen mixture (ozone: 0.016 mmol s^{-1}, oxygen: 3.3 cm^3 s^{-1}) on 0.136 mmol of **1a** in 10 ml of solvent. b) Yield was based on **1a** reacted. c) The value of ratio N/C attack was based on **4a**/**2a**.

TABLE 2. SUBSTITUENT EFFECT ON THE OZONIZATION OF TRIPHENYLMETHANE DYE a)

Run	Substrate	Ozone consumed / 10^{-4} mol	Substrate reacted / 10^{-4} mol	Yield b)/%				Ozone (consumed) / Substrate (reacted)	N/C c) attack
				2	**3**	**4**	**6**		
1	**1c**	0.44	0.42	26	0	0	23	1.1	0
2	**1a**	0.40	0.34	7	1	47	10	1.2	6.7
3	**1b**	0.41	0.32	1	3	60	4	1.3	60
4	**1d**	0.30	0.18	trace	trace	72	5	1.7	∞

a) Ozonization was carried out with an ozone-oxygen mixture (ozone: 0.016 mmol s^{-1}, oxygen: 3.3 cm^3 s^{-1}) on 0.136 mmol of substrate in 10 ml of methanol at 0 °C. b) Yield was based on the substrate reacted. c) The value of ratio N/C attack was based on **4**/**2**.



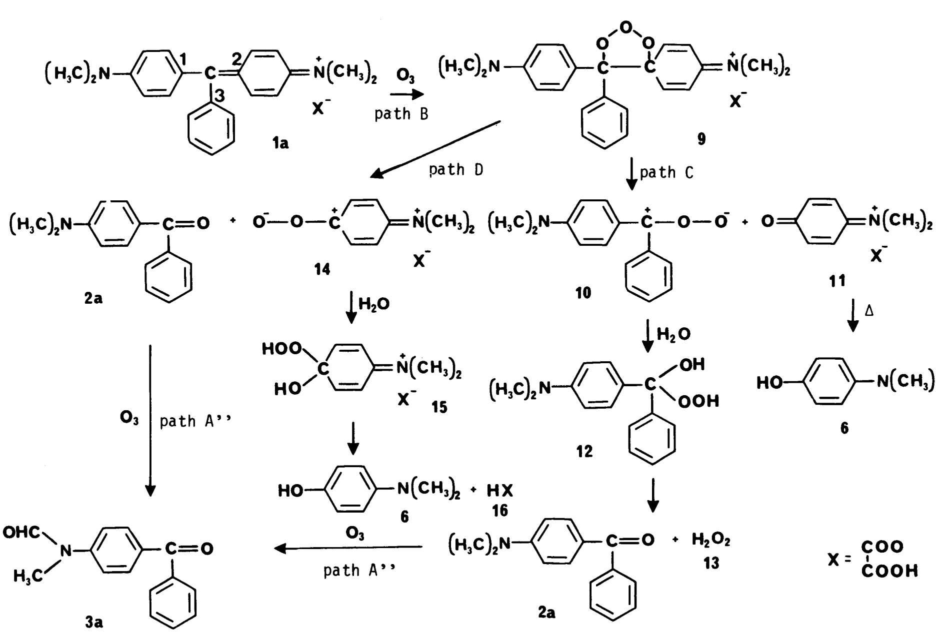
Scheme 1.

tertiary-amines.[21,22] Ozone electrophilically attacks the dimethylamino nitrogen to give **1a**-ozone adduct **7**, which is converted into *N*-hydroxymethyl-*N*-methylamino derivative **8** [path A]. Since the value of the ratio ozone(consumed)/substrate(reacted) of **1d**, whose dimethylamino moiety is preferentially attacked by ozone was 1.7 (Table 2, run 4), it was concluded that the *N*-hydroxymethyl-*N*-methylamino derivative **8** is further ozonized to give the *N*-formylmethylamino derivative **4a**. Some radical process in which an oxygen molecule takes part may be involved. The *N*-formylmethylamino derivative **4a** is further ozonized to give either *N*,*N*′-diformylmethylamino derivative **5a** [path A′] or the ketone **3a** and *p*-(dimethylamino)phenol (**6**) [path B′]. The *N*,*N*′-diformylmethylamino derivative **5a** is further ozonized to give the ketone **3a** [path B″].

A mechanism for the ozone attack on the skeleton of **1a** is proposed in Scheme 2. Except for the primary ozonides of α,β-unsaturated carbonyl compounds, certain allylic compounds, and certain substituted cinnamic esters, primary ozonides decompose into the corresponding carbonyl oxides and carbonyl compounds.[23] In Scheme 2, carbons C1 and C2 are considerably more negative than carbon C3, due to the mesomeric effect produced by the dimethylamino groups. When ozone electrophilically attacks C1 and C2, a primary ozonide **9** is formed [path B]. The direction of the cleavage of the primary ozonide **9** follows two possible paths. The primary ozonide **9** can cleave to carbonyl oxide **10** and ketone **11** [path C]. The carbonyl oxide **10** reacts with water to give 4-(dimethylamino)benzophenone (**2a**) and hydrogen peroxide (**13**) *via* hydroperoxide **12**. The ketone **11** can be converted into *p*-(dimethylamino)phenol (**6**) at the injection room of the gas chromatograph during analysis.

In contrast, the primary ozonide **9** can decompose to 4-(dimethylamino)benzophenone (**2a**) and carbonyl oxide **14**, which reacts with water to give *p*-(dimethylamino)phenol (**6**) and oxalic acid (**16**) *via* hydroperoxide **15** [path D].

In fact, the presence of a small amount of water (*ca.* 0.2%) was confirmed by gas chromatography. In order to differentiate path C from path D, the following experiments were carried out. If the primary ozonide **9** had cleaved by path C, hydrogen peroxide (**13**), which is formed from the hydroperoxide **12**, should have been detected. Unfortunately, it was impossible to differentiate the hydrogen peroxide (**13**) from the peroxides formed by the ozonization of methanol which was used as a solvent. On the other hand, if the primary ozonide **9** had cleaved by path D, the phenolic proton of *p*-(dimethylamino)phenol would have come from the water. The relative yield of *p*-(dimethylamino)phenol-*d* for *p*-(dimethylamino)phenol produced by the ozonization of **1a** in the presence of heavy water is shown in Fig. 2. For a greater ratio of heavy water, the relative yield of *p*-(dimethylamino)phenol-*d* also increased. However, this result does not sufficiently prove that the primary ozonide **9** cleaves mainly by path D. Since even in the presence of *ca.* 70 molar equivalents of heavy



Scheme 2.

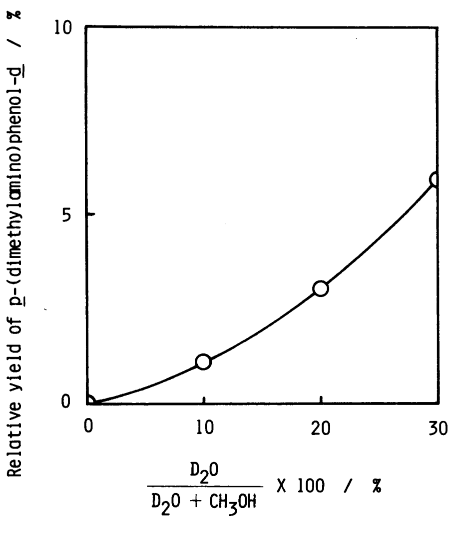


Fig. 2. Relative yield of *p*-(dimethylamino)phenol-*d* in the ozonization of **1a**.

water (30%), only 6% of *p*-(dimethylamino)phenol-*d* was observed. It was thus concluded that the primary ozonide **9** mainly cleave by way of path C and to a lesser extent by way of path D. The result is consistent with the general rule that a primary ozonide cleaves to a carbonyl oxide whose carbocation is more liable to be stabilized by the mesomeric effect.[24] 4-(Dimethylamino)benzophenone (**2a**) was further ozonized to give 4-(*N*-formylmethylamino)benzophenone (**3a**) [path A''].

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