Synthesis and characterisation of an intermediate in the peroxyoxalate chemiluminescence: 4-chlorophenyl *O*,*O*-hydrogen monoperoxyoxalate

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The peroxyoxalate system undergoes one of the most efficient chemiluminescence reactions and is the only one supposed to involve an intermolecular chemically induced electron exchange luminescence mechanism, with proven high efficiency. Several reactive intermediates are proposed in the literature, which, upon interaction with an activator dye, lead to excited state generation. In this work, we report the synthesis, spectral characterisation and chemiluminescence properties of 4-chlorophenyl *O*,*O*-hydrogen monoperoxyoxalate (1), a compound analogous to one of the proposed reactive intermediates. In the presence of the activator dye 9,10-diphenylanthracene (DPA) alone, 1 does not exhibit any chemiluminescence emission. This fact eliminates compounds of this type as possible reactive intermediates in the peroxyoxalate reaction. However, the addition of various bases [*i.e.* imidazole, potassium *tert*-butoxide, potassium *p*-chlorophenolate and 1,8-bis(dimethylamino)naphthalene] to 1 in the presence of DPA results in high intensity light emission.

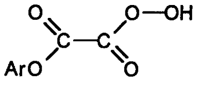
Introduction

The peroxyoxalate system remains one of the most efficient chemiluminescent processes,[1,2] exhibiting luminescence quantum yields (Φ_{CL}) of up to 0.3 Einstein mol^{-1} (1 Einstein = 1 mol of photons). It consists of a base catalysed reaction between activated oxalic phenyl esters and hydrogen peroxide, in the presence of highly fluorescent aromatic hydrocarbons, having low oxidation potentials (E_{ox}), as chemiluminescent activators (ACT). The excited state generation in this system is believed to involve the 'chemically induced electron exchange luminescence (CIEEL)' mechanism,[3] a widely accepted mechanism for chemiluminescent peroxide decomposition.[4]

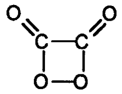
More recently, doubts about the efficiency of the CIEEL mechanism in the diphenoyl peroxide decomposition (a CIEEL system *par excellence*) arose from a redetermination[5] of Φ_{CL}, which proved to be three orders of magnitude lower than the previously reported[6] value. Therefore, the peroxyoxalate reaction is the only chemiluminescent system, supposed to involve an *intermolecular* CIEEL mechanism, with proven high efficiency, as indicated by a recent careful determination of the quantum yield.[2] Nevertheless, it should be mentioned here that a highly efficient excited state generation supposed to proceed by an *intramolecular* CIEEL-like mechanism has been reported.[7] However, the peroxyoxalate system represents the most adequate model for the study of the *intermolecular* CIEEL mechanism.

The mechanism of this complex reaction is still not well understood, especially in regard to the excitation step, the elementary step in which the electronically excited state of the activator is formed. Rauhut[1] postulated 1,2-dioxetanedione (**II**) as the high-energy intermediate responsible for ACT excitation. Other possible reactive intermediates (**I**, **III** and **IV**) have also been proposed in subsequent kinetic studies,[8-13] although on the basis of rather indirect evidence only.

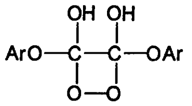
The most direct evidence on the structure of the reactive intermediate comes from a ^{19}F NMR spectral study on the reaction of bis(2,6-difluorophenyl) oxalate with hydrogen peroxide, in the presence of an activator.[12] The authors proposed a peracid analogous to **I** as the most probable reactive intermediate, capable of excited state generation, upon interaction with the activator.



I



II



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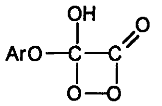


IV

On the basis of a recent kinetic study from our laboratory, we have proposed a simplified mechanistic scheme for the peroxyoxalate chemiluminescence and still favour dioxetanedione (**II**) as the reactive intermediate structure, although our suggestion is only supported by indirect evidence.[14] In this work, we report the synthesis, characterisation and chemiluminescent properties of a possible intermediate of the peroxyoxalate chemiluminescence, namely of 4-chlorophenyl *O*,*O*-hydrogen monoperoxyoxalate, an analogue of the peracid intermediate **I**. We show that such a derivative is not the reactive intermediate which leads to light generation upon direct interaction with an activator. Therefore, we have direct evidence which allows the elimination of **I** as a possible reactive intermediate structure in the peroxyoxalate chemiluminescence.

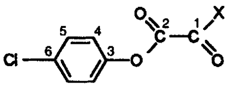
Results

Synthesis

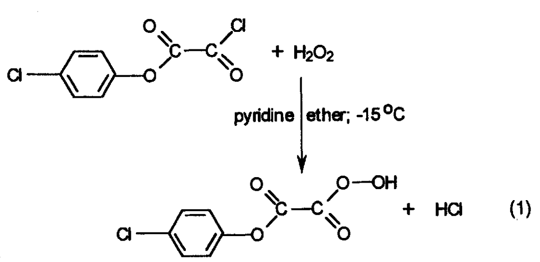
The reaction of oxalyl monochloride 4-chlorophenyl ester [4-chlorophenyl (chloroformyl)formate] with hydrogen peroxide in the presence of pyridine, at −15 °C, yielded a relatively stable peroxide [R_F = 0.55, on SiO$_2$ in CH$_2$Cl$_2$–hexane–acetonitrile (15:3:2) at −20 °C, monitored iodometrically], which was attributed to 4-chlorophenyl *O*,*O*-hydrogen monoperoxyoxalate (**1**) [eqn. (1)].

After low temperature work-up, a white solid was obtained (mp *ca.* 0 °C). This product still contained considerable amounts of 4-chlorophenyl hydrogen oxalate (**2**) (R_F = 0.12)

Table 1 INVGATE ^{13}C NMR data and assignments for **1** and **2**[a]

	C-1	C-2	C-3	C-4	C-5	C-6
1	154.6 (0.90)	156.3 (0.67)	149.3 (1.00)	123.8 (2.03)	130.4 (2.17)	132.4 (1.12)
2	158.5 (1.02)	157.8 (0.91)	149.6 (1.00)	123.9 (1.88)	130.3 (1.95)	132.1 (1.17)

[a] δ Values in ppm relative to tetramethylsilane (TMS) and relative integral intensities in parentheses, −10 °C, [$^2H_6$]acetone, 50 MHz; **1**: X = -OOH; **2**: X = -OH.



(1)

and 4-chlorophenol (**3**) ($R_F = 0.85$) as impurities. Further attempts to purify the product by flash column chromatography on either silica gel, alumina or Florisil, with various CH_2Cl_2–hexane mixtures at −40 °C, resulted in complete decomposition of the peroxide. This is not altogether surprising, as Bartlett and Pincock[15] have observed the high susceptibility of alkyl peroxyoxalates towards decomposition upon attempted purification by column chromatography.

4-Chlorophenyl hydrogen oxalate (**2**) was synthesised as a reference compound, in an analogous way, by substituting hydrogen peroxide for water, and was obtained in a pure enough form (>95%) as judged by quantitative ^{13}C NMR spectroscopy (inverse-gated decoupling method).[16]

Characterisation

Inverse-gated decoupling[16] (INVGATE) ^{13}C NMR spectroscopic experiments, which allow integration, performed at −10 °C in [$^2H_6$]acetone, show the presence of three products in the reaction mixture. Two of them can readily be identified as **2** and **3**, by comparison with the spectra of authentic samples and the third one is attributed to the peracid **1** (Table 1) for the following reasons. (i) In the ester/acid carbonyl region, four peaks are observed, two of which correspond to the acid **2** (158.5 and 157.8 ppm). The other two signals (156.3 and 154.6 ppm) should correspond to the ester and hydroperoxy carbonyls of the peracid **1** (see below). (ii) These assignments are in good agreement with the fact that, in [$^2H_6$]acetone, the ^{13}C NMR spectrum of *m*-chloroperbenzoic acid (MCPBA) presents the perhydroxycarbonyl carbon signals 2.0 ppm upfield relative to the carboxy carbon signals of the corresponding acid (MCBA).[†] (iii) Addition of KI, which reduces peroxides, causes the complete disappearance of all the signals assigned to the carbons of the peracid **1**, while the peaks due to **2** and **3** remain unchanged. (iv) The addition of imidazole, which catalyses the chemiluminescent decomposition of **1** (see below), also leads to the complete disappearance of the peaks attributed to **1**, together with a substantial concomitant reduction in the intensity of the peaks due to **2**[‡] and a corresponding increase in the intensity of the free phenol absorptions. It is noteworthy, that no more peroxide is detected in the sample after the imidazole addition. (v) In the aromatic carbon region, pairs of signals, separated by 0.1 to 0.3 ppm, are observed for **1** and **2**, apart from the easily attributed signals due to free phenol **3**. The assignment of the signals due to acid and peracid, respectively (Table 1), was performed by comparison with the spectrum of authentic **2**, from the relative integral intensities and with the aid of the experiments outlined in (iii) and (iv).

The infrared spectrum of the reaction product in CCl_4 solution at room temperature shows two carbonyl absorptions at 1753 and 1768 cm^{-1}, originating from the acid **2** and the peracid **3**, respectively, and a very broad O–H stretching band at *ca.* 3600 cm^{-1} due to both **2** and **3**. The spectrum of a neat film revealed, besides the bands observed in solution, an absorption at 1458 cm^{-1}, which may correspond to the O–H bending of the peracid.[18]

Mass spectrometry, in direct injection mode, of an ethereal solution of the product reveals, albeit with low intensity, the molecular peaks of **1** at *m*/*z* 216/218 (in a 3:1 ratio), corresponding to the natural abundance of ^{35}Cl and ^{37}Cl in $C_8H_5O_5Cl$.

Chemiluminescence emission

The reaction product in ethyl acetate leads to a bright chemiluminescence emission in the presence of imidazole ($pK_a = 6.95$) and 9,10-diphenylanthracene (DPA) as activator, readily observable by the naked eye. In contrast, when the base catalyst imidazole is omitted there is no light emission at all. Also in the presence of pyridine ($pK_a = 5.25$) no light emission is observed; however with potassium *p*-chlorophenolate ($pK_a = 9.2$), 1,8-bis(dimethylamino)naphthalene ($pK_a = 12.34$) and potassium *tert*-butoxide ($pK_a \approx 18$) a strong light emission is obtained.

Fig. 1 shows the kinetics of light emission observed with the different bases. It is important to emphasise again the lack of any detectable light emission in the absence of base. The light emission kinetics are accompanied by the release of 4-chlorophenol, as shown by the observation of its absorption at 292 nm. The kinetic curve of phenol release with imidazole as base is also shown in Fig. 1. It should be pointed out here that the reaction product used for the chemiluminescence tests does not contain any hydrogen peroxide (as judged by thin layer chromatography, developed with KI solution) or oxalyl monochloride 4-chlorophenyl ester (excluded by exhaustive washing with cold saturated aqueous ammonium chloride), which could react with each other, leading to light emission in the presence of DPA.

Discussion

Our results confirm the successful synthesis of 4-chlorophenyl *O*,*O*-hydrogen monoperoxyoxalate (**1**). Indications as to the structure of **1** were obtained by TLC, IR and mass spectrometry, however, the most important evidence is supplied by INVGATE ^{13}C NMR spectroscopy. The spectroscopic data of **1** when compared with that of **2**, as well as the decomposition of **1** under the conditions of the chemiluminescence experiments and upon iodide addition, confirm the

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[†] A solvent effect is certainly involved here, because, in deuteriochloroform, the perhydroxy carbonyl carbon of MCPBA appears 2.9 ppm downfield of the carboxy carbon of MCBA[17] (data not shown).

[‡] In agreement with this observation, on monitoring 4-chlorophenol release, it was verified that the peracid **1** reacts 40 times faster with imidazole than the acid **2** (data not shown).

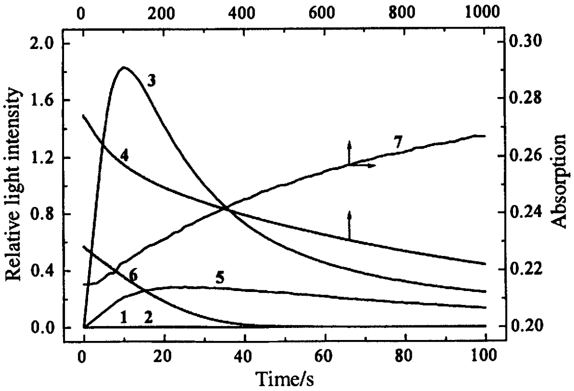

Fig. 1 Light emission kinetics and phenol release in the reaction of 4-chlorophenyl *O*,*O*-hydrogen monoperoxyoxalate with several bases in the presence of DPA. *Light emission* 450 nm. **1**, [**1**] = 0.10 mmol dm^{-3}, [DPA] = 1.0 mmol dm^{-3}, absence of base, ethyl acetate; **2**, [**1**] = 0.10 mmol dm^{-3}, [DPA] = 1.0 mmol dm^{-3}, [pyridine] = 1.0 mmol dm^{-3}, ethyl acetate; **3**, [**1**] = 0.50 mmol dm^{-3}, [DPA] = 1.0 mmol dm^{-3}, [potassium *p*-chlorophenolate] = 0.70 mmol dm^{-3}, THF; **4**, [**1**] = 0.10 mmol dm^{-3}, [DPA] = 1.0 mmol dm^{-3}, [imidazole] = 1.0 mmol dm^{-3}, ethyl acetate; **5**, [**1**] = 1.0 mmol dm^{-3}, [DPA] = 1.0 mmol dm^{-3}, [1,8-bis(dimethylamino)naphthalene] = 1.0 mmol dm^{-3}, ethyl acetate (relative light intensity × 10); **6**, [**1**] = 0.50 mmol dm^{-3}, [DPA] = 1.0 mmol dm^{-3}, [$\mathrm{Bu^tOK}$] = 3.0 mmol dm^{-3}, THF; *4-Chlorophenol release*, absorption at 292 nm. **7**, [**1**] = 0.10 mmol dm^{-3}, [imidazole] = 1.0 mmol dm^{-3}, ethyl acetate.

structure of peracid **1**.[§] The assignments of the observed signals to the carbons C-1 and C-2 of peracid **1** and acid **2** (Table 1) merit some further comments. Even using a recycle delay time of 40 s, we were not able to attain full relaxation conditions for the peaks at 156.3 and 157.8 ppm (see integrals in Table 1). Empirically, one can argue that C-1 and C-2 should relax mainly by a combination of the chemical shift anisotropy and spin-rotation mechanisms.[19] While the former mechanism should produce similar relaxation in both carbons, the latter, as it depends on internal rotation, should be most efficient for the terminal carbon (C-1). Thus we assign those signals to the C-2 of **1** and **2**, respectively. Furthermore, this assignment results in the expected similarity of the chemical shift values for the ester carbons (C-2) of **1** and **2**.

The most important result obtained from our preliminary studies on the chemiluminescence properties of the peracid **1** is the observation that it does not interact directly with the activator DPA to emit light (Fig. 1) but, instead, **1** is stable in presence of DPA. This fact clearly excludes intermediates of the type **I** as reactive intermediates[¶] in the peroxyoxalate chemiluminescence, in striking contrast to the conclusions obtained in a recent literature report.[12] However, upon treatment with a base of pK_a > 6, light emission is observed in the presence of DPA, which establishes that the present peracid **1** is able to generate excited states.

With potassium *p*-chlorophenolate and $\mathrm{Bu^tOK}$, the sequence is initiated by fast deprotonation, followed by cyclization to the reactive intermediate, which, upon interaction with the activator, leads to excited state generation. In this case, the kinetically observed step should correspond to the cyclization of the peracid anion. The kinetically observed step with 1,8-bis(dimethylamino)naphthalene[‖] should be the slow proton transfer from **1** to the hindered base. With imidazole on the other hand, nucleophilic catalysis[14] should be involved, and the slow step is supposed to be the imidazole attack on the ester moiety of **1**.

In conclusion, our results suggest that, independent of the nature of the base utilised, the peracid **1** has to suffer a relatively slow chemical transformation, supposed to be a cyclization to a four-membered ring peroxide, to yield the reactive intermediate, which is capable of excited state generation upon interaction with an activator. Consequently, it was not possible to observe kinetically the excitation step. Nevertheless, we are able to exclude, based on direct evidence, the peracid structure **I** as a reactive intermediate in the peroxyoxalate chemiluminescence.

Experimental

Chemicals

4-Chlorophenol (98% Merck) was recrystallised from a mixture of light petroleum and toluene and dried under vacuum. Oxalyl chloride (99% Aldrich) and imidazole (99% Aldrich) were used as received. Pyridine (99% Aldrich) was refluxed for 4 h over NaOH and then distilled. Oxalyl monochloride 4-chlorophenyl ester was prepared according to the literature procedure.[21] The product distilled at 120 °C/10 mmHg, yielding a white solid (52%, mp 45 °C); δ_C(50 MHz, $CDCl_3$) 121.9, 129.4, 132.9, 148.2, 153.7, 160.4. Ethyl acetate, used in the kinetic assays, was purified by the following procedure. The ethyl acetate was left to stand over $CaCl_2$, for 1 d, stirred for 30 min over NaOH (40 g dm^{-3}) at 0 °C, allowed to stand for 1 d over 4 Å molecular sieves, and then carefully distilled (bp 77 °C) and stored under nitrogen over freshly dehydrated 4 Å molecular sieves.

Apparatus

Chemiluminescence measurements were performed on a SPEX-Fluorolog 1681 spectrofluorimeter (slit: 2.5 mm, emission wavelength: 450 nm, photomultiplier voltage 750 kV), absorption measurements were performed on a HITACHI U-2000 spectrophotometer, the infrared spectra were obtained on a Perkin-Elmer FT-IR 1750 spectrophotometer, the NMR analyses on a Bruker AC 200-F spectrometer (50 MHz for ^{13}C) and the mass spectrometry on a Finnigan Mat INCOS 50 mass spectrometer.

4-Chlorophenyl *O*,*O*-hydrogen monoperoxyoxalate (1)

An anhydrous hydrogen peroxide solution in diethyl ether was prepared by extracting 20 cm^3 of a 60% aqueous H_2O_2 solution with diethyl ether (3 × 15 cm^3). The combined diethyl ether layers were dried extensively with anhydrous magnesium sulfate and the peroxide concentration of the resulting solution determined iodometrically.[22]

A solution of oxalyl monochloride 4-chlorophenyl ester (600 mg, 2.7 mmol), in 10 cm^3 of anhydrous diethyl ether, was added dropwise during 20 min to a 5.0 mol dm^{-3} anhydrous ethereal

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[§] An alternative structure for **1** might be the peranhydride [ClC_6H_4O–C(O)–C(O)–O–]$_2$ (**4**), which could have properties similar to those of **1**. Indeed, an additional peroxidic compound was detected (TLC, R_F = 0.75) on using excess of oxalyl monochloride 4-chlorophenyl ester in the preparation. However, on using excess of H_2O_2, only one peroxidic compound (R_F = 0.55) is obtained, which should correspond to the peracid **1**. Additionally, a compound having the structure **4** is not supposed to give rise to the above mentioned 216/218 molecular peaks observed in the MS.

[¶] It should be pointed out clearly what we call a reactive intermediate. It is that one of the various possible intermediates in the peroxyoxalate reaction, which, upon interaction with the activator—probably involving the CIEEL sequence—leads to the generation of the activator's singlet excited state. Of course, peracids **I** are intermediates in the peroxyoxalate reaction, by the way common to all mechanistic schemes proposed till now,[1,8–14] but they are not 'reactive intermediates'.

[‖] The observation of light emission with 1,8-bis(dimethylamino)-naphthalene contributes to establishing the structure of **1**. This strong and extremely hindered base possesses two outstanding properties:[20] an extremely slow proton transfer rate constant and an almost complete lack of nucleophilicity. In view of these facts, such a base would not be able to liberate the peracid anion from the hypothetical peranhydride. Therefore, the experiments with this base exclude once more the above mentioned peranhydride **4** as a possible alternative structure for compound **1**.

solution of hydrogen peroxide (5.0 cm^3, 25 mmol) and pyridine (0.24 cm^3, 2.7 mmol), under dry nitrogen. After 30 min of stirring at -15 °C, the mixture was washed with cold saturated aqueous ammonium chloride (3 × 15 cm^3) and the diethyl ether layer dried over magnesium sulfate for 10 min at 0 °C. The solvent was evaporated at a temperature below -10 °C and a white solid obtained (mp ~0 °C). Thin layer chromatography (TLC) on SiO_2, at -20 °C, using CH_2Cl_2–hexane–acetonitrile (15:3:2) as eluent showed three substances with $R_F = 0.12$, 0.55 and 0.85, respectively. The spot at $R_F = 0.55$ was peroxidic (10% aqueous KI) and the others appeared as red spots when revealed with Methyl Orange (in water–ethanol, 9:1). Flash chromatography was performed on silica gel 60 at -40 °C, using the above solvent mixture, but no peroxidic compound could be eluted. Further attempts at purification, using alumina and Florisil, in the same conditions, also led to complete peracid decomposition.

The infrared spectra were obtained by fast insertion of a CCl_4 solution containing the product into an IRTRAN-2 cell, followed by acquisition at room temperature. Another spectrum was obtained by adding a drop of an ethereal solution of the product between KCl plates and acquisition after solvent evaporation. $\nu_{max}(CCl_4)/cm^{-1}$ 1753, 1768 (ν, C=O), 3607 (ν, O–H); $\nu_{max}(neat)/cm^{-1}$ 1458 (δ, O–H), 1765 (ν, C=O), 3567 (ν, O–H) (ν = stretching, δ = bending).

4-Chlorophenyl hydrogen oxalate (2)

A solution of oxalyl monochloride 4-chlorophenyl ester (300 mg, 1.4 mmol), in 10 cm^3 of anhydrous diethyl ether, was added dropwise during 20 min to an ethereal solution of water (0.40 cm^3, 22.2 mmol) and pyridine (0.11 cm^3, 1.4 mmol). After 30 min of stirring with the temperature kept between -15 and -20 °C, the mixture was washed with cold saturated aqueous ammonium chloride (3 × 15 cm^3) and the diethyl ether layer dried with magnesium sulfate for 10 min at 0 °C. The solvent was evaporated at a temperature below -10 °C and a white solid obtained. TLC on SiO_2, at -20 °C, using CH_2Cl_2–hexane–acetonitrile (15:3:2) as eluent showed one substance with $R_F = 0.12$.

^{13}C NMR spectroscopic data

All spectra were acquired using the standard Bruker program INVGATE.AU (recycle delay: 40 s; acquisition time: 1.3 s; pulse duration: 2.0 µs [34°]; 32 k data points). The data were then zero filled to 64 k data points and Fourier transformed under matched filter conditions. The digital resolution was *ca.* 0.4 Hz per data point.

The spectroscopic data for the peracid **1** and the acid **2** are shown in Table 1.

4-Chlorophenol $\delta_C(-10$ °C, [$^2H_6$]acetone, 50 MHz) 117.5 (C-2), 124.0 (C-3), 129.8 (C-4), 157.0 (C-1).

m-Chlorobenzoic acid $\delta_C(-10$ °C, [$^2H_6$]acetone, 50 MHz) 128.8 (C-6), 129.9 (C-5), 131.2 (C-2), 133.5 (C-4), 133.5 (C-1), 134.6 (C-3), 166.7 [C(O)OH].

m-Chloroperbenzoic acid $\delta_C(-10$ °C, [$^2H_6$]acetone, 50 MHz) 128.2 (C-6), 129.3 (C-5), 131.6 (C-2), 134.3 (C-4), 134.3 (C-1), 135.0 (C-3), 164.7 [C(O)OOH].

Chemiluminescence emission

The chemiluminescence tests were initiated by fast injection of an ethyl acetate stock solution of **1** (15 µl, 100 mmol dm^{-3}, determined iodometrically)[22] to 3.0 cm^3 of a DPA solution in ethyl acetate in absence and presence of base {[**1**] = 0.50 mmol dm^{-3}, [DPA] = 1.0 mmol dm^{-3}, [pyridine] = [imidazole] = [1,8-bis(dimethylamino)naphthalene] = 1.0 mmol dm^{-3}}. Light emission was observed visually or with a fluorimeter. The experiments using potassium *p*-chlorophenolate and Bu^{t}OK as the base were performed in tetrahydrofuran; to avoid humidity a cuvette closed with a septum was used ([*p*-chlorophenolate] = 0.70 mmol dm^{-3}, [Bu^{t}OK] = 3.0 mmol dm^{-3}).

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