optical activity and structure is known, as in the case of polarimetric detectors, but indeed this limitation is overcome by using empirical or nonempirical rules, which directly relate the sign of the CD to the absolute configuration. Even if the above correlations have to be used carefully (in particular those which require the use of sector rules), it is to be expected that current progress in theoretical interpretation of CD data will make the present approach increasingly reliable and applicable.

In summary, the possibility of determining elution order constitutes a basis for investigation of chiral discrimination mechanisms and helps to clarify at least the most important interactions in the chiral recognition. In addition, when preparative HPLC systems are used for the separation of enantiomers it is possible to assign at the same time absolute configuration and optical purity to the fractions eluted from the absorption and CD detection. This will be of great practical importance because it will allow one to test immediately important molecular properties, like biological ones, which are often strongly dependent on absolute stereochemistry.[4]

Experimental Section

Materials. Compounds Ia and II were commercial samples from Fluka and were used without further purification. Compounds Ib and Ic were prepared by Al-*i*-Bu_3 and $LiAlH_4$ reduction of the corresponding ketones, respectively. Compounds III and IV were prepared from the corresponding alcohols (Jansen) by using standard procedures.

Chromatographic Resolutions. The separations were carried out by means of a Jasco Twinckle apparatus. The absorption was obtained by means of a UVIDEC-100V detection, whilst the CD detection was provided by Jouan II dichrograph or a JASCO J500C spectrometer equipped with a micro HPLC cell. The Pirkle column (i.e., (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine ionically bonded to a commercial 5 μm γ-aminopropylsilanized silica column from Merk, Darmstadt, West Germany) was prepared in situ, following the procedure reported.[11] The mobile phase was hexane containing up to 5% isopropyl alcohol. The poly(trityl methacrylate) was prepared and coated on phenylsilanized silica as reported by Yuki, Okamoto, et al.[12] In this case the eluent was methanol.

Acknowledgment. We wish to thank Professors G. Giacomelli and R. Lazzaroni for providing us with samples of Ib and Ic, respectively. Particular thanks are due to Prof. W. H. Pirkle, for his constructive criticism in refereeing this paper.

Registry No. Ia, 98-85-1; Ib, 611-69-8; Ic, 3835-64-1; II, 602-09-5; III, 1460-57-7; IV, 92720-77-9.

Kinetics and Mechanism of the Oxidation of Aromatic Aldehydes by Hexachloroiridate(IV)

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The kinetics of oxidation of benzaldehyde and some substituted benzaldehydes by hexachloroiridate(IV) have been studied spectrophotometrically in the visible region. The reaction is first order in benzaldehyde and in iridium(IV). The influence of acidity on the reaction is small. The activation parameters of the reaction have been calculated. The oxidation reaction is found to have a deuterium isotope effect, k_H/k_D, of 7.0, indicating that the cleavage of the C–H bond of the aldehyde is the rate-determining step. The reaction appears to be of outer-sphere type and occurs through the intermediate formation of free radicals.

Introduction

The oxidation of some organic compounds such as phenols,[1] quinols,[2] alcohols,[3,4] and neutralized α-keto[5] and α-hydroxy acids[6] by hexachloroiridate(IV) has been studied. The kinetics and mechanism of the oxidation of some aliphatic and aromatic aldehydes by some other oxidants have been studied.[7,8] In some cases the mechanistic approach has been based on intermediate ester formation[8] between the substrate and the oxidant followed by the decomposition of the ester to give products; in other cases the results have been interpreted by the intermediate formation of free radicals[7c] followed by the reaction of the free radical with the oxidant to give products. The present investigation on the oxidations of aromatic aldehydes by hexachloroiridate(IV) was carried out in view of the results reported earlier with other oxidants.[7,8]

Experimental Section

Reagents. Glacial acetic acid of BDH (AnlaR) was heated under reflux for 6 h with excess of $K_2Cr_2O_7$ and distilled just before use. The solution of benzaldehyde in water was made by delivering a known volume of freshly distilled (under inert atmosphere) benzaldehyde from a calibrated pipette. The aldehydes were purified by distillation under reduced pressure just before use. Benzaldehyde exhibited an absence of peroxide by starch iodide test and no red coloration with $FeSO_4$–NH_4SCN reagent. A solution of benzaldehyde in sodium acetate–acetic acid buffer was worked up for benzoic acid in the same manner as shown in product analysis. It indicated that the amount of benzoic acid was less than 0.5% in a freshly prepared solution and remained

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almost unchanged even on standing for three months at room temperature in a stoppered bottle. Thus the possibility of aerial oxidation to benzoic acid under the kinetic condition has been ruled out.

Preparation of PhCDO.[9a] The reaction between benzil (mp 95 °C, 10 g in 200 mL of dry ether) and lithium aluminium deuteride (1.1 g in 50 mL of dry ether) with stirring at 20 °C for 4 h followed by treatment with excess of Rochelle salt solution and the usual workup furnished dihydrobenzoin-d_2 (9.7 g): mp 118–120 °C; ^{1}H NMR (60 MHz) δ ($CDCl_3$) 2.2 (1 H, broad, OH) and 7.2–8.0 (5 H, complex multiplet, aromatic H). To the stirred mixture of lead tetraacetate (90%, 25 g in 100 mL of dry benzene) was added dropwise at 20 °C a solution of dihydrobenzoin-d_2 (9.0 g in 300 mL of dry benzene). Water was added to the reaction mixture after 6 h and the usual workup furnished a pale yellow oil which distilled at 175–178 °C as a colorless oil (5.5 g): IR ν_{max} (film) 2100 and 2050 cm^{-1} (reported[9a] 4.76 and 4.83 μm); ^{1}H NMR δ (CCl_4) 7.2–7.9 (complex multiplet, aromatic H), no signal for the aldehyde H.

All the solid inorganic materials were of reagent grade and all solutions were prepared in doubly distilled water. $Na_2IrCl_6 \cdot 6H_2O$ (Johnson–Mathey) was used as the source of iridium(IV). Standardization of iridium(IV) was effected spectrophotometrically. The absorption spectrum of iridium(IV) showed the maximum at 488 nm and minimum at 462 nm in sodium acetate–acetic acid buffer. Beer's law has been found to be valid at 488 nm in the concentration range studied. The $IrCl_6^{3-}$ salt or its hydrolyzed product $IrCl_5(H_2O)^{2-}$ is nearly transparent at 488 nm.

Kinetic Measurements. A large excess of aromatic aldehydes was used for all kinetic measurements. The rate of decrease of iridium(IV) was followed in a Perkin-Elmer (digital) spectrophotometer with a cell of path length of 1 cm at 488 nm. The reaction was studied in the presence of sodium acetate–acetic acid buffer. Generally 10–15 experimental points were taken in each run. Good straight lines were obtained for at least two half-lives. The pseudo-first-order rate constants were calculated from the logarithm of absorbance vs. time plots. The rate constants were reproducible to within ±3%.

Product Analysis and Stoichiometry. The estimation of unreacted benzaldehyde through the 2,4-DNP derivative was irksome and gave inconsistent results. Therefore the following method was adopted for the isolation of benzoic acid (the product) which was estimated by titration with standard sodium hydroxide.

The reaction mixture was extracted with chloroform (AR, distilled, 3 × 25 mL). The combined organic layer was washed with distilled water (10 mL) and then extracted with saturated aqueous $NaHCO_3$ solution (2 × 10 mL). The chloroform extract was dried (Na_2SO_4) and on removal of the solvent furnished a neutral oily residue which was characterized as benzaldehyde (unreacted) through the 2,4-DNP, mp 235 °C dec. The combined alkaline extract was acidified (congo-red) with concentrated HCl and the precipitated organic acid was extracted again with chloroform (3 × 10 mL). The combined organic layer was washed with water (2 × 5 mL) and dried (Na_2SO_4). On removal of the solvent, a colorless residue was obtained, mp 121 °C, which remained undepressed on admixture with authentic benzoic acid. Acetic acid was completely absent in the product which was left under vacuum for 2 h before estimation.

It was observed that 20 mL of the freshly prepared stock solution of benzaldehyde in acetic acid–sodium acetate buffer contained 3 mg of benzoic acid which remained practically unaltered in the course of three months (estimated every fortnight). This stock solution (20 mL) was treated with 20.8 mg of iridium(IV) and the reaction was monitored spectrophotometrically till iridium(IV) was almost completely (99%) consumed. The reaction mixture on workup by the aforementioned method gave the total quantity of benzoic acid (5.1 mg) indicating that 20.8 mg of iridium(IV) produced 2.1 ± 0.2 mg of benzoic acid. The theoretical yield of PhCOOH from 20.8 mg of iridium(IV) becomes 2.3 mg which is in fairly good agreement with the observed value. This experiment which was repeated several times with two and four times as much iridium(IV) as necessary resulted in the proportional increase in benzoic acid formation. All these suggest a stoichiometry of 2 mol of $IrCl_6^{2-}$ per mole of benzaldehyde as shown below.

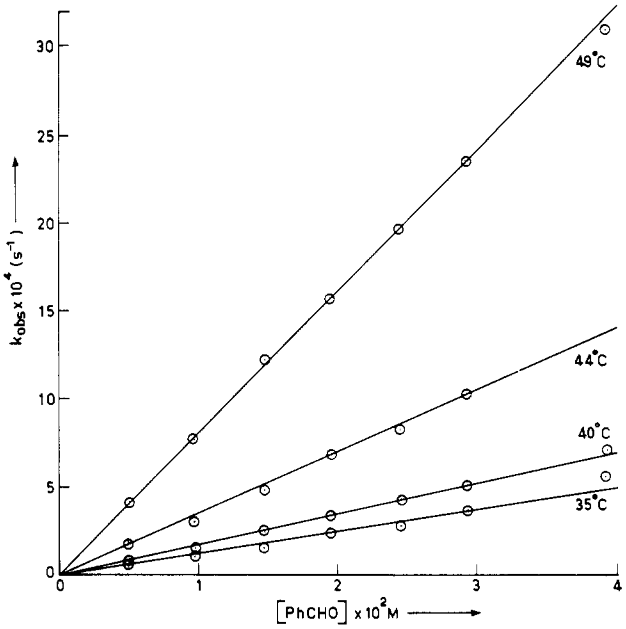

Figure 1. Influence of substrate concentrations on pseudo-first-order rate constants. Plots of k_{obsd} vs. [PhCHO]. [Ir(IV)] = 1.30 × 10^{-4} M; pH 4.27.

Table I. Effect of Salts on the Pseudo-First-Order Rate Constants[a]

	$k_{obsd} \times 10^4$, s^{-1}		
[salts], M	NaCl	$NaClO_4$	Na_2SO_4
0	4.42	4.42	4.42
0.05	5.67	5.94	6.40
0.1	6.39	7.07	7.41
0.2	7.68	7.99	8.72
0.3	9.12	9.24	9.59
0.5	11.7	12.2	12.60

[a] [PhCHO] = 9.8 × 10^{-3} M; [Ir(IV)] = 1.65 × 10^{-4} M; pH 4.27; temperature 46 °C.

$$PhCHO + 2Ir(IV) + H_2O = PhCOOH + 2Ir(III) + 2H^+$$

Iridium(III) products, e.g., $IrCl_6^{3-}$ and $IrCl_5(H_2O)^{2-}$, were determined following the procedure of Cecil and his co-workers.[1] After kinetic experiments iridium(III) products were reoxidized by passing dry and HCl-free chlorine for 2 h through the solution and the absorbancies of the resulting solution were measured at 460 and 487 nm. When the extinction coefficients of $IrCl_6^{2-}$ and $IrCl_5(H_2O)^-$, at these wavelengths, were used, the concentrations of the respective iridium(III) species were then calculated. These indicate that $IrCl_6^{2-}$ is mainly reduced to $IrCl_6^{3-}$ (>90%).

Results

Effect of Reactant Concentrations. The reaction was investigated at varying concentrations of iridium(IV) and fixed concentrations of other reactants. The pseudo-first-order rate constants are independent of Ir(IV) concentrations (0.39–2.47) × 10^{-4} M. The effect of variation of benzaldehyde on the pseudo-first-order rate constant was studied at constant [Ir(IV)] and a pH of 1.3 × 10^{-4}M and 4.27, respectively. The plots of k_{obsd} vs. [substrate] are linear passing through the origin at different temperatures (Figure 1), indicating that the reaction is first order in each [Ir(IV)] and [PhCHO].

Effect of Iridium(III). The reaction was studied in the presence of different iridium(III) concentrations

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Table II. Influence of Acetic Acid Concentration on the Pseudo-First-Order Rate Constants[a]

% HOAC (v/v)	$k_{obsd} \times 10^5$, s^{-1}
0	18.2
5	10.2
10	7.14
15	3.07
20	1.77

[a] [Ir(IV)] = 1.08×10^{-4} M; [PhCHO] = 9.8×10^{-3} M; pH 4.27; temperature 30 °C.

(conditions the same as in Table I). The pseudo-first-order rate constant was independent of iridium(III) concentrations even when iridium(III) was added initially in the ratio of [Ir(III)]/[Ir(IV)] = 10. This excludes the possibility of a back reaction between the free radical and iridium(III).

Effect of pH. Reactions were carried out at [PhCHO], [Iridium(IV)], ionic strength, and temperature of 9.8×10^{-3} M, 1.7×10^{-4} M, 0.1 M, and 46 °C, respectively. The rate of oxidation appears to be unchanged at lower pH values (<3.0). However, an increase in rate was observed when the pH of the solution was increased from 3.23 to 4.63. No experiments have been carried out at pH above 4.63 because of the rapid reduction of $IrCl_6^{2-}$ by OH^- in basic solution.[11b] The reaction of $IrCl_6^{2-}$ with OH^- does not contribute to the reaction in this study as the pH is well below that where the reaction is significant. A 3-fold increase in pseudo-first-order rate constant for a change in pH from 3.23 to 4.63 was observed.

Effect of Salts. The reaction was also investigated in the presence of different salts such as sodium perchlorate, sodium chloride, and sodium sulfate (Table I). The pseudo-first-order rate constant increases with an increase in all these salt concentrations although the rate is slightly faster in sodium sulfate than in sodium chloride or sodium perchlorate. This is possibly because the ionic strength of a sodium sulfate solution is much higher than that of sodium chloride or sodium perchlorate of equal concentration. A linear relationship was observed when $\log k_{obsd}$ was plotted against μ (ionic strength) indicating that the reaction takes place between an ion and an uncharged molecule.[12b]

Effect of Solvent Composition. The rate of oxidation of benzaldehyde was studied in the presence of different concentrations of acetic acid. The pseudo-first-order rate constants listed in Table II indicate that the rate increases with the decrease in acetic acid content (v/v) in the reaction mixture. Moreover, the rate is sufficiently larger in lower acetic acid concentrations to indicate that hydrated benzaldehyde[7-9] participates in the reaction with iridium(IV).

Effect of Substituents. The pseudo-first-order rate constant was determined by using benzaldehyde and substituted benzaldehydes under comparable conditions. Since some of the substituted aldehydes are highly insoluble in water all these runs were taken in 5% (v/v) acetic acid medium. Contrary to the observations made earlier in chromic acid[7] and bromate ion[8] oxidations of aromatic aldehydes it has been noted in the present study that the rate of the reaction increases considerably when methoxybenzaldehydes are used and the reverse is the case with nitrobenzaldehydes. The pseudo-first-order rate constant increases to the extent of 70% in *o*-methoxybenzaldehyde whereas decreases to nearly 68% in *o*-nitrobenzaldehyde. Similar observations have also been made in meta- and para-substituted methoxy- and nitrobenzaldehydes.

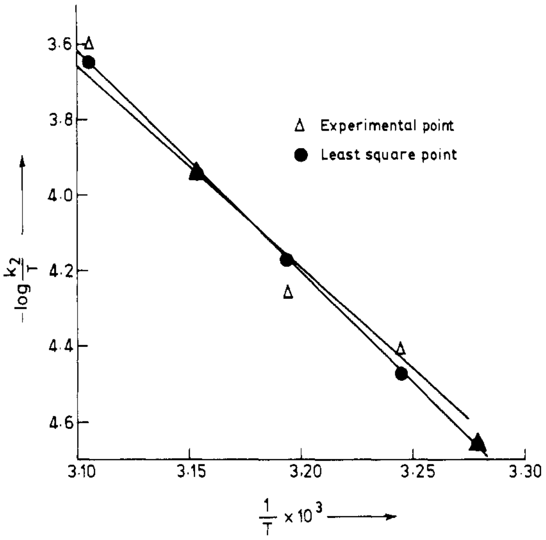

Figure 2. Variation of second-order rate constants with temperature. Plot of $\log k_2/T$ vs. $1/T$.

Effect of Temperature. The values of second-order rate constants were calculated at different temperatures. A least-square treatment of the data was used to obtain the best straight line and the enthalpy of activation ($\Delta H^{\ddagger}$) was calculated[10a] from the plot of $\log k_2/T$ against $1/T$ (Figure 2) followed by the calculation of entropy of activation ($\Delta S^{\ddagger}$). The reaction is characterized by high enthalpy of activation and an equivalently large positive entropy of activation.[10b] The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 112.0 kJ mol^{-1} and 81.2 J K^{-1} mol^{-1}, respectively.

Deuterium Isotope Effect. The observed deuterium isotope effect in benzaldehyde-d_1 are incorporated in Table III. The pseudo-first-order rate constants decreased considerably more in benzaldehyde-d_1 than benzaldehyde under comparable conditions of the experiment. The isotope effect, k_H/k_D of 7.0 is very close to the normal value predicted for the breaking of one C–H bond.[9]

Effect of Vinyl Compounds. The pseudo-first-order rate constants were determined in the presence of vinyl compounds (conditions the same as in Table I). The pseudo-first-order rate constants are 4.42×10^{-4}, 3.82×10^{-4}, 3.53×10^{-4}, and 3.38×10^{-4} (s^{-1}) at acrylamide concentrations of 0, 1.4×10^{-2}, 2.8×10^{-2}, and 4.2×10^{-2} M, respectively, whereas the values are 4.42×10^{-4}, 3.02×10^{-4}, 2.57×10^{-4}, and 2.30×10^{-4} (s^{-1}) at comparatively higher acrylonitrile concentrations of 0, 1.5×10^{-1}, 3.0×10^{-1}, and 4.5×10^{-1} M, respectively. It is suggested that polymer when formed[11a] may preferentially adsorb one of the reactants thereby decreasing its bulk concentration and hence the reaction rate in solution. The above experiments were further corroborated by the polymerization test which was performed at the acrylamide concentration of 1.5 M in the mixture and at pH 4.0. The substrate (1 mL) was added to 1 mL of 9.8×10^{-2} M iridium(IV). The total volume was adjusted to 10 mL. A white suspension was immediately noticeable when a large excess of methanol was added to the reaction mixture. Control experiments from which either iridium(IV) or aldehdye was excluded gave no detectable polymers. All these indicated the production of free radicals in the solution.

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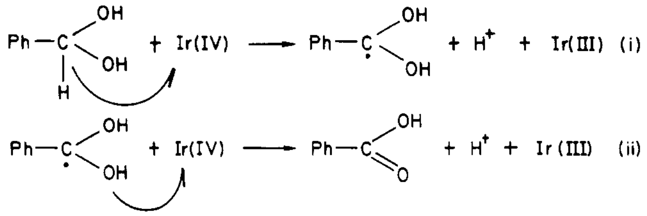
Table III. Deuterium Isotope Effect of the Reaction at 30 °C[a]

[substrate] × 10^3, M	$k_H \times 10^4$, s^{-1}	$k_D \times 10^4$, s^{-1}	k_H/k_D
6.0	1.14	0.162	7.0
8.0	1.48	0.215	6.9
9.8	1.82	0.260	7.0

[a] [Ir(IV)] = 1.128×10^{-4} M; pH 4.27; temperature 30 °C.

Discussion

The kinetic data do not indicate the formation of intermediate 1:1 complex between the substrate and iridium(IV). The reaction is strictly first order with respect to both iridium(IV) and benzaldehyde. Hexachloroiridate(IV) is known to be stable[12] toward substitution or hydrolysis over a wide range of acidities. On the other hand, photochemical behavior of $IrCl_6^{2-}$ which has been studied[13] in the ultraviolet region indicated that aquation of $IrCl_6^{2-}$ leading to the formation of $IrCl_5(H_2O)^-$ takes place only at the high acidity (~6.0 M) and high iridium(IV) concentrations of 0.5–2.0 M. Since the reaction has been studied at lower acidities (pH 4.27) and iridium(IV) concentrations of ~10^{-4} M, it is believed that $IrCl_6^{2-}$ and not $IrCl_5(H_2O)^-$ oxidizes benzaldehyde. Again aliphatic aldehydes are known to be rapidly and substantially hydrated[14,15] in aqueous solution. Evidence for hydration as a stage before the reaction with bromine has also been shown in the oxidation of benzaldehyde by different workers.[7-9] It is suggested that hydrated aldehyde reacts with iridium(IV). Though hydride transfer has been shown to occur in bromine oxidation of aldehydes,[16] the removal of hydrogen as hydride ion from the hydrated aldehyde by iridium(IV) seems unlikely in the present study since iridium(IV) is primarily a one-electron transfer oxidant. In connection with the oxidation of some diols by this oxidant, the reactions have been shown to occur through the initial rupture of the O–H bond and large energies of activation, 149–164 kJ mol^{-1}, have been obtained.[4] On the other hand, when iridium(IV) initially attacks a C–H bond of alkanols, comparatively smaller activation energies, 80–121 kJ mol^{-1}, are required.[3] Moreover, in the oxidation of the enol form of cyclohexanone by this oxidant where intermediate free radical is obtained by breaking the O–H bond, a substantial primary isotope effect of $k(D_2O)/k(H_2O) = 2.5$ has been observed by Cecil and his co-workers,[1] whereas in the present study the reaction seems to be slightly faster in normal water than in deuterium oxide and the ratio $k(H_2O)/k(D_2O)$ is 1.1. The results (k_H/k_D) recorded in Table III further corroborate this contention that iridium(IV) initially attacks the C–H bond of hydrated benzaldehyde to give free radical and iridium(III) followed by the reaction of the free radical with another iridium(IV) to give products as follows.



The step i is expected to be rate determining, and step ii to be a fast reaction of the transient free radical with a second iridium(IV) to yield benzoic acid. Both steps i and ii may be assisted by the electrophilic nature of iridium(IV), and hereby the outer-sphere reaction process is not contradicted. The isolation of benzoic acid in almost quantitative yield indicates that benzil, PhCOCOPh is not produced in this oxidation and provides further support for a very fast reaction of the free radical with iridium(IV) to yield benzoic acid. An alternative two-step process involving formation of unhydrated radical $Ph—\dot{C}=O$ followed by reaction with H_2O and iridium(IV) can easily be ruled out.

In connection with the electron-transfer oxidation of some organic compounds by hexachloroiridate(IV) Cecil and his co-workers[1] have shown that chloro derivatives of the organic compounds are formed and some of these reactions have been shown to occur partly by outer-sphere and partly by inner-sphere mechanisms. Although aromatic aldehydes are readily converted to aroyl halides[17] on treatment of halogens, nuclear halogenation[18] can be accomplished in moderate yield without oxidation of the aldehyde provided that the aldehyde is complexed with $AlCl_3$ before addition of halogen, that no solvent is used, and that sufficient $AlCl_3$ is present to complex with halogen. The present reaction was carried out in aqueous medium and in the absence of any catalyst. Thus the possibility of nuclear halogenation was remote, and no evidence for chlorinated products from the oxidation of benzaldehyde was detected by mass spectrometry. These facts support the conclusion that the present reaction occurs mainly by an outer-sphere mechanism.

Acknowledgment. Thanks are due to C.S.I.R. and U.G.C. (New Delhi) for awarding a fellowship and associateship to S. Dey and S. Sen Gupta, respectively. Thanks are also due to Dr. B. C. Das, Institut De Chimic Des Substances Naturelles (CNRS), Gif-Sur-Yvette, France, for the mass spectrum.

Registry No. Na_2IrCl_6, 16941-25-6; PhCDO, 3592-47-0; D_2, 7782-39-0; benzaldehyde, 100-52-7; *o*-methoxybenzaldehyde, 135-02-4; *o*-nitrobenzaldehyde, 552-89-6; *m*-methoxybenzaldehyde, 591-31-1; *p*-methoxybenzaldehyde, 123-11-5; *m*-nitrobenzaldehyde, 99-61-6; *p*-nitrobenzaldehyde, 555-16-8; benzil, 134-81-6; dihydrobenzoin-d_2, 36239-19-7.

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