129. *The Inhibition of Acetaldehyde Oxidation by Hydrocarbons of Various Molecular Structures.*

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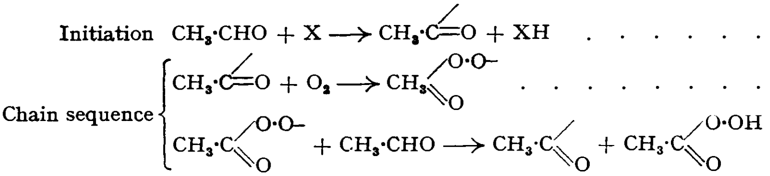
The method of crossed reaction chains for testing for correspondence between different oxidation mechanisms has been extended. Various hydrocarbons were mixed with the system $CH_3{\cdot}CHO + O_2 + N_2$ (1 : 3·7 : 8·6) undergoing oxidation at 150—250°. The inhibition observed with the *n*-paraffins pentane, hexane, and heptane was found to increase with increasing chain length. In the C_5 series *iso*pentane was a more powerful inhibitor than *n*-pentane, and with pent-2-ene even more pronounced inhibition was observed.

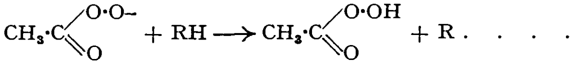
This inhibition is attributed to a non-regenerative crossing with the acetaldehyde oxidation chain



Initiation $CH_3{\cdot}CHO + X \longrightarrow CH_3{\cdot}\overset{/}{C}{=}O + XH$ . . . . . . (1)

Chain sequence $\left\{\begin{array}{l} CH_3{\cdot}\overset{/}{C}{=}O + O_2 \longrightarrow CH_3{\cdot}C\begin{smallmatrix}O{\cdot}O-\\ O\end{smallmatrix} \\ CH_3{\cdot}C\begin{smallmatrix}O{\cdot}O-\\ O\end{smallmatrix} + CH_3{\cdot}CHO \longrightarrow CH_3{\cdot}C\begin{smallmatrix}/\\ O\end{smallmatrix} + CH_3{\cdot}C\begin{smallmatrix}O{\cdot}OH\\ O\end{smallmatrix} \end{array}\right.$ . . . . (2) (3)

such that the third step is replaced by



$CH_3{\cdot}C\begin{smallmatrix}O{\cdot}O-\\ O\end{smallmatrix} + RH \longrightarrow CH_3{\cdot}C\begin{smallmatrix}O{\cdot}OH\\ O\end{smallmatrix} + R$ . . . . (4)

(where RH is a hydrocarbon molecule)

At the temperatures studied, the R radical appears to be unable to continue a fruitful oxidation chain. Examination of the reaction products suggests that this radical becomes stabilised almost entirely as an olefin. Thus the crossing of the reaction chains at (4) leads to inhibition.

The fact that pent-2-ene is more effective in reaction (4) than the *n*-paraffins accords with the greater ease of abstraction of hydrogen from a methylene group in the α-position to the double bond. The greater inhibitory power of *iso*pentane than of *n*-pentane may likewise be attributed to the lower energy of rupture of the tertiary C–H bond. The correlation of inhibiting power with chain length in *n*-paraffins parallels the ease of oxidation of these molecules at higher temperatures and is tentatively attributed to facilitation of reaction (4) by the increased contribution from vibration coupling in the longer hydrocarbons. Some auto-solvent effects may also result from the increased molecular flexibility of the longer paraffin chains.

THE temperature required for uncatalysed oxidation reactions in gaseous paraffins is about 250°, and is so high that the more labile reaction intermediates have only a transient life. They are difficult to detect in the oxidation products and there is therefore considerable speculation concerning the reaction mechanism. For this reason any method of promoting reaction chains at temperatures where the identification of these labile intermediate becomes possible constitutes a major contribution towards the elucidation of controversial points in the slow combustion of paraffin hydrocarbons.

A possible method for inducing oxidation reactions in paraffins involves the method of crossed reaction chains (Small and Ubbelohde, *J.*, 1950, 723). In the previous investigation various hydrocarbons were introduced into an acetaldehyde–air mixture undergoing vigorous oxidation at temperatures below 200°. At these temperatures the hydrocarbons themselves are inert towards molecular oxygen under the conditions of the experiment. The results showed that no oxidation chains for the hydrocarbons investigated could cross fruitfully with those of acetaldehyde. In some cases, however, the added hydrocarbon had a detectable inhibitory influence in the aldehyde system. This inhibition was interpreted on the basis of hydrogen transfer from the paraffin, which was thought to stabilise aldehyde peroxide radicals so that they could no longer propagate their own reaction chains. Reactions of the type (4) (above) were suggested.

This interpretation implies the liberation of alkyl radicals in the aldehyde system, but at the temperatures used the evidence was against the establishment of a subsequent hydrocarbon oxidation chain such as:

$$R + O_2 \longrightarrow RO_2 \qquad (2')$$

$$RO_2 + RH \longrightarrow RO{\cdot}OH + R \qquad (3')$$

It has now been verified that inhibition of the aldehyde oxidation by *n*-pentane is accompanied by the production of olefinic material.

An interesting influence of molecular structure on the efficiency of inhibition was suggested by the previous observations. This feature has been further studied. By use of a new reaction vessel and flow rates comparable to those employed previously, it has been established that *n*-pentane, *n*-hexane, and *n*-heptane in equal molecular quantities produce an inhibition on the aldehyde oxidation which increases with chain length in the paraffin. With the other hydrocarbons tested, results indicate a sequence of increasing inhibiting effects in the order *n*-pentane < *iso*pentane < *n*-hexane < *n*-heptane < pent-2-ene.

As is discussed below, structural changes in the hydrocarbon molecule may facilitate the transfer of hydrogen from the hydrocarbon to the aldehyde peroxide radical and thus account for the relative inhibitory efficiencies observed. The greater ease of transfer from an olefin agrees with other knowledge about the ease of disruption of C–H bonds in the α-position to an olefinic bond. The increasing ease of transfer with increasing length of the *n*-paraffin chain parallels certain features of hydrocarbon oxidation.

EXPERIMENTAL

The reaction tube shown in Fig. 1 was similar to that already described by us (in the press), but different methods were used for the collection of reaction products. It was constructed of Pyrex tubing 45 cm. long and had an internal diameter of 3·8 cm. This combustion tube was surrounded by a close-fitting steel furnace heated electrically. Reaction temperatures were recorded axially in the gas flow.

Before entering the combustion chamber the reacting gases were mixed by turbulent flow through closely packed Pyrex chips and glass wool. The reaction mixture consisted essentially of two gas streams whose flow rates were determined by calibrated flow-meters. One of these was nitrogen (approx. 10 c.c./sec.) which passed through a carburettor of acetaldehyde kept in a thermostat at 0° and carried aldehyde molecules into the furnace. The second gas stream was air, which was passed into the reaction tube at a measured rate to supply a source of molecular oxygen for the combustion. When it was desired to study the effects of various paraffins in the aldehyde system, the hydrocarbons were held in separate carburettors kept in thermostats at temperatures such as to give a partial pressure of 280 mm. and were transported to the combustion chamber in the air stream.

The basic reaction taking place in all cases was the oxidation of acetaldehyde, and the aim was to maintain substantially constant conditions for the oxidation except in so far as these became modified by the presence of added diluents.

According to analytical requirements the combustion products were either collected in bubblers (Fig. 1) or were isolated by rapid chilling in collection vessels (Fig. 1*a*) immersed in carbon dioxide and alcohol. Normally two such traps were used in series.

In view of possible explosion hazards, all combustion reactions took place behind protective screens composed of Perspex and strong steel mesh. When oxidation is extensive, considerable accumulations of organic peroxides can occur and this necessitates the observance of similar precautions in working with undiluted condensates. In practice, thermal explosions were occasionally observed, but these were very mild and only occurred when combustion was in active progress.

Preparation of Materials.—Acetaldehyde. This was obtained by distillation from paraldehyde, a few drops of dilute sulphuric acid being used as depolymerising agent. Gentle warming of the distillation flask on a water-bath prevented excessive charring. The aldehyde was freshly distilled for each run, shielded from strong light, and protected from oxidation by a current of dry, oxygen-free nitrogen.

n-*Pentane.* Because of the special influence of unsaturation it was particularly desirable to remove all traces of unsaturated material from the commercial grades of paraffin hydrocarbons. *n*-Pentane was stored for several weeks over 20% oleum with occasional shaking. The hydrocarbon obtained by decantation was washed with potassium hydroxide and then gently refluxed for 24 hours with a concentrated solution of the same reagent. Repeated washing with water and drying (Na_2SO_4) completed the purification process. This procedure also assisted removal of branched-chain isomers which are more readily sulphonated than *n*-pentane.

Fractional distillation under oxygen-free nitrogen in a 16″ column packed with porcelain rings gave a cut, b. p. 35—36°, n_D^{18} 1·3580, which was used in these experiments.

n-*Hexane.* This was purified in the same way as *n*-pentane. Fractional distillation gave a sample, b. p. 67·5—68·5°, n_D^{18} 1·3810. A carburettor at 41° gave a partial pressure of 280 mm.

n-*Heptane.* This was purified as for *n*-pentane and -hexane. Distillation gave a fraction, b. p. 95·5—97°, n_D^{18} 1·3995. A thermostat at 68° gave a partial pressure of 280 mm.

FIG. 1.

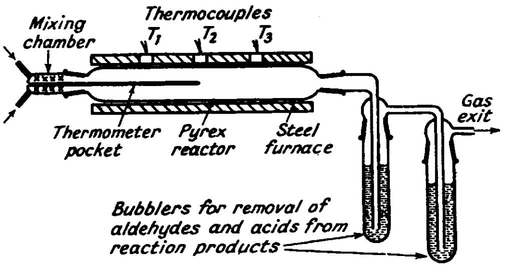
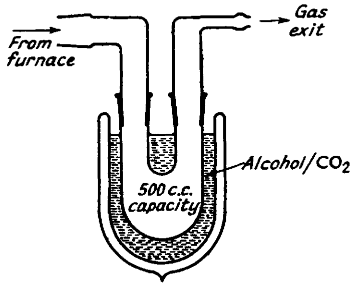


FIG. 1*a*.



Pent-2-ene. This was distilled, b. p. 35—36°/753 mm., n_D^{18} 1·3839, and used without further purification. A carburettor at 6·5° gave p = 280 mm.

iso*Pentane.* Owing to the easier attack of *iso*-hydrocarbons by oleum, a different procedure was used for the separation of any olefins in the sample of commercial *iso*pentane. Blank experiments showed that, whereas olefins of the chain lengths likely to be present were very rapidly brominated when shaken with dilute bromine water, substitution of the bromine into the saturated hydrocarbons was only just perceptible after 24 hours. Light and air were excluded as far as possible, and the commercial *iso*pentane was briefly shaken with bromine water, then immediately washed several times with concentrated sodium hydroxide. The hydrocarbon was distilled through a tube of sodium hydroxide pellets steam-jacketed at 100° to ensure complete removal of hydrogen bromide and organic bromides. The product, collected in a cooled receiver, was fractionated before use, and had b. p. 27°, n_D^{18} 1·3561.

Preparation of Reaction Vessel.—To ensure uniform surface conditions in all experiments, the reaction tube was thoroughly cleaned with equal volumes of concentrated nitric and sulphuric acid at 100° before each run. Abundant washing with water, then distilled water, and drying at 200° completed the cleaning process.

Analysis of Reaction Products.—The general procedure was identical with that described previously (*J.*, 1950, 725). When hydrocarbon had been added to the aldehyde oxidation, the condensate separated into two layers. The hydrocarbon layer was washed with water, and the washings were added to the aqueous layer. The entire aqueous product was then made up to 250 ml. and titrated for peroxide, aldehyde, and acid content by standard procedures. When the bubblers were used, the aqueous scrubbings were made up as a standard solution which could be analysed for reaction products.

Results.—General characteristics of the aldehyde oxidation. The combined yield of peroxide and acid is plotted as a percentage of the aldehyde used in the oxidation in Figs. 2 and 3. Before the addition of hydrocarbon molecules the reaction tube was calibrated with an acetaldehyde–air mixture corresponding with the reference mixture in the Table below. Fig. 2, curve *A*, plots the general course of oxidation. A smooth curve is obtained showing a steep rise at 190°. Ignition and mild explosion of the reaction mixture occurred at temperatures above 205°. Slow combustion was always accompanied by production of a thin white mist from the exit tube. Curve *B* records the effect of diluting the reference mixture with nitrogen, in proportions similar to those used for the hydrocarbon diluents.

In several of these reference experiments the combustion tube was packed with broken Pyrex chips. Three points (*F*) in Fig. 2 show how the reaction is completely suppressed at temperatures where thermal explosion was observed with the same mixture in an unpacked vessel. At about 250° a reaction then appeared to start and led to the production of a faint mist at the exit tube. An immediate temperature rise to 260°, followed by a further increase to 280°, was probably the result of intense but localised reaction. About 10% of oxidation was obtained, but since the reaction temperature was completely uncontrollable this result is not plotted. This inhibition of oxidation by increasing the extent of surface in the vessel will not be discussed in detail here. It seems unlikely that the inhibitions observed on addition of hydrocarbons can be due to wall effects.

Fig. 2.

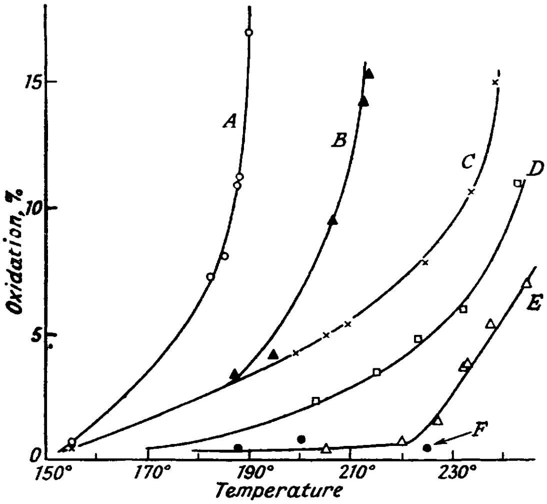
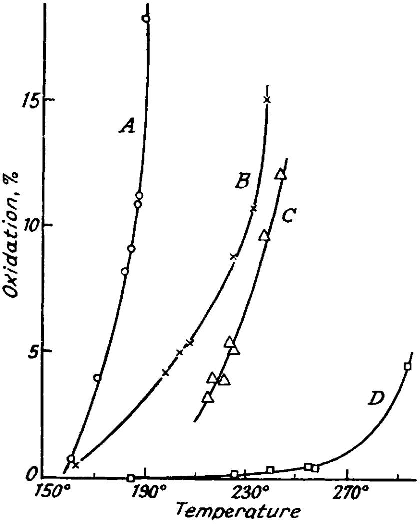


Fig. 3.



Effect of hydrocarbons on the aldehyde oxidation. In this work the aims were to keep essentially constant conditions for the aldehyde oxidation, and to add hydrocarbons in comparable molecular proportions. The extent to which these aims were realised is illustrated in Table 1. It will be observed that for each of the additions the total molar rate of gas flow remained substantially constant during the series. The experimental results plotted in Figs. 2 and 3 show that the percentage of aldehyde oxidised is appreciably reduced in the presence of the paraffin molecules studied.

Table 1. (Flow rates in g.-mols./sec. × 10^3.)

Mixture : $CH_3 \cdot CHO$ plus	$CH_3 \cdot CHO$	O_2	N_2	Hydrocarbon	Total flow rate
(Ref. mixture) Figs. 2 and 3, *A* ...	0·348	0·0937	0·803	Absent	1·245
N_2, Fig. 2, *B*	0·348	0·0937	0·803	0·276(N_2)	1·512
C_5H_{12}, Fig. 2, *C* ; Fig. 3, *B*	0·348	0·0937	0·803	0·284	1·514
C_6H_{14}, Fig. 2, *D*	0·348	0·0937	0·803	0·295	1·517
C_7H_{16}, Fig. 2, *E*	0·348	0·0937	0·803	0·276	1·516
C_5H_{10}, Fig. 3, *D*	0·348	0·0937	0·803	0·255	1·500
iso-C_5H_{12}, Fig, 3, *C*	0·348	0·0937	0·803	0·264	1·509

Under the conditions of these experiments the saturated hydrocarbons do not themselves undergo appreciable oxidation below about 250°. The marked and specific reduction in overall oxidation when nitrogen is replaced by hydrocarbons, which is observed from as low as 150° upwards, thus cannot be due to attack of the hydrocarbon on molecular oxygen competing with the attack of acetaldehyde on oxygen. It seems likely that the hydrocarbon breaks a proportion of the oxidation chains of the acetaldehyde, by collisions with one of the chain carriers leading effectively to chain termination.

When *n*-paraffins inhibit the oxidation of acetaldehyde it is particularly desirable to determine whether the observed effects are primarily physical, such as the promotion of energy-removing collisions with varying efficiency according to the structure of the hydrocarbon, or whether chemical changes in the hydrocarbon molecule explain the effects observed. To test this point a detailed chemical analysis was carried out on *n*-pentane recovered from the condensing traps. The hydrocarbon material was repeatedly washed with water until the last washings gave negative reactions with Schiff's reagent. Normally only a few washings were required before all water-soluble aldehydes were removed. After being dried (Na_2SO_4) the hydrocarbon was divided into two samples. One sample was carefully fractionated; no evidence could be obtained for the formation of long-chain aldehydes such as valeraldehyde in the residues of fractionation. The other sample was tested for olefins, a sensitive method of analysis being necessary. Blank experiments were made on synthetic mixtures of pent-2-ene and *n*-pentane. The general procedure was to add excess of standard solution of bromine in carbon tetrachloride to a mixture, and store it in the dark in a stoppered vessel. The extent of bromine absorption was determined volumetrically at various time intervals. It was verified that the bromine reacted very rapidly in the presence of any unsaturated material but only very slowly (by substitution) with the *n*-hydrocarbon.

When this procedure was used with recovered pentane, the sample showed a slight but definite bromine absorption, indicating that some of the *n*-pentane used had been converted into olefinic material. Typical results are recorded in Table 2. Measurements of refractive indices were also carried out on the same hydrocarbon samples. The figures given above confirm the formation of olefins in the recovered material, but refractive indices are insufficiently sensitive for definite measurements in view of the small amounts of unsaturation involved.

TABLE 2. *Bromine values of hydrocarbon solutions.*

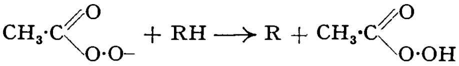
Hydrocarbon	n_D^{18}	Time of contact with Br_2, hr.	Bromine absorbed, %
Pure *n*-pentane	1·3580	1	0
		4½	0
		50	0·104
n-Pentane + ⅛% of amylene (Synthetic mixture)	1·3590	½	0·428
		1	0·412
		26	0·437
Recovered hydrocarbon (washed and dried)	1·3590	½	0·246
		4½	0·247
		16½	0·294

DISCUSSION

The main result from the present study of crossed reaction chains in the oxidation of acetaldehyde is to confirm that a number of molecules which might be expected to propagate oxidation actually act as inhibitors. One striking illustration from the figures is that this inhibition changes what would be a thermal explosion around 200° to a slow combustion.

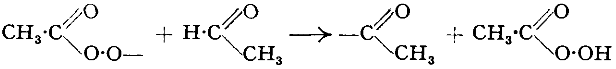
The influence of molecular structure on inhibiting efficiency is noteworthy. The range of molecules so far studied gives a suggestive though not a complete picture. When the information available is combined with other results on the oxidation mechanism and on the influence of structure on hydrocarbon reactivity, certain problems can be focused more sharply.

(i) The production of olefins from paraffins, accompanying the inhibition process, suggests that this is closely associated with transfer of hydrogen from the hydrocarbon molecules to a chain carrier in the oxidation of acetaldehyde. This hypothesis was suggested in our earlier publication (*J.*, 1950, 723) and has been adopted recently by Farmer and McDowell (*Trans. Faraday Soc.*, 1952, **48**, 624) to explain the inhibitory effect of alcohols in the oxidation of acetaldehyde. The fact that pentene is much more efficient than the *n*-paraffins as an inhibitor supports this suggestion, since the C–H bond proximate to C=C is known to be more readily disrupted than in a paraffin (Farmer, *ibid.*, 1942, **38**, 348). The greater inhibition by *iso*pentane than of *n*-pentane also appears to be due to the lower energy of disruption of the tertiary C–H bond in *iso*pentane. On the basis of the reaction scheme outlined above, the chemical aspect of the inhibition can be formulated as :



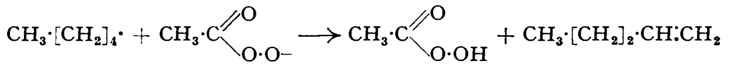
$$\mathrm{CH_3{\cdot}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O{\cdot}O{-}}\end{array} + \mathrm{RH} \longrightarrow \mathrm{R} + \mathrm{CH_3{\cdot}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O{\cdot}OH}\end{array} \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

competing with



$$\mathrm{CH_3{\cdot}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O{\cdot}O{-}}\end{array} + \mathrm{H{\cdot}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{CH_3}\end{array} \longrightarrow \mathrm{{-}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{CH_3}\end{array} + \mathrm{CH_3{\cdot}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O{\cdot}OH}\end{array}$$

At the temperatures used, the R radicals in (4) are unable to propagate the chain efficiently, so that partial inhibition of the oxidation of the acetaldehyde results. The subsequent fate of these R radicals is to produce olefins, possibly by disproportionation : $2\mathrm{R} \longrightarrow \mathrm{RH} + \mathrm{R'{\cdot}CH{:}CH_2}$, or by other chain-terminating reactions such as



$$\mathrm{CH_3{\cdot}[CH_2]_4{\cdot}} + \mathrm{CH_3{\cdot}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O{\cdot}O{-}}\end{array} \longrightarrow \mathrm{CH_3{\cdot}C}\begin{array}{l}{/\!\!/}\mathrm{O}\\ \backslash\mathrm{O{\cdot}OH}\end{array} + \mathrm{CH_3{\cdot}[CH_2]_2{\cdot}CH{:}CH_2}$$

The yields of olefins so far obtained are definite but too small to permit detailed chemical analysis.

(ii) The marked efficiency of hydrogen as an inhibitor (Small and Ubbelohde, *Nature*, 1951, **168**, 201 ; and results in the press) and the increasing efficiency of paraffin inhibition as the chain lengthens suggest that energy removal in collisions with an activated chain carrier may also be important in the inhibition. As discussed elsewhere (Ubbelohde, *Proc. Roy. Soc.*, 1935, *A*, **152**, 354 ; Small and Ubbelohde, *locc. cit.*) for the case of hydrocarbon oxidation, the processes in the oxidation chain

$$\mathrm{RH} + \mathrm{X} \longrightarrow \mathrm{XH} + \mathrm{R} \quad \text{or} \quad \mathrm{RO_2} + \mathrm{RH} \longrightarrow \mathrm{RO{\cdot}OH} + \mathrm{R}$$

are thermoneutral or endothermic, whereas (2) (above) and $\mathrm{R} + \mathrm{O_2} \longrightarrow \mathrm{RO_2}^*$ are exothermic. Further reaction of the energy-rich $\mathrm{RO_2}^*$ will occur most easily before this exothermic energy is dissipated by collisions. It seems likely that hydrogen is particularly efficient in deactivating $\mathrm{RO_2}^*$. The increased range of coupled vibrations in the *n*-paraffins with increasing chain length might be playing a similar rôle in facilitating energy transfer in deactivating collisions such as $\mathrm{RO_2}^* + \mathrm{RH} \longrightarrow \mathrm{RO_2} + (\mathrm{RH})^*$. Collisions of this type could also be favoured by the crumpling of the *n*-paraffins (cf. Ubbelohde, *Rev. Inst. franc. Pétrole*, 1949, **4**, No. 9, 488) which in the limit makes the energy transfer similar to that in a solvent (the " auto-solvent effect "). These aspects of the reactivity of hydrocarbons are under further investigation.

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