Use of Solvents in the Low-Pressure Plasma Oxidation of Olefins

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The oxidation of n-octene has been studied in mixtures with dimethylbutane, 1,4-dimethylcyclohexane, ethylcyclohexane, and dibutyl ether. Except for dimethylbutane, total yields increase on addition of a solvent, and the fraction of epoxide among the products is higher than in reactions with neat octene.

1. INTRODUCTION

Organic compounds in the plasma of a glow discharge undergo a variety of transformations. In fortunate cases these can be used in chemical synthesis[1]; however, more often the primary products of such reactions are hot and undergo fragmentations and rearrangements leading to complex product mixtures. Far greater selectivities have been achieved in heterogeneous reactions of plasmas with liquid surfaces. In order to prevent competing gas-phase reactions, such processes can only be carried out with liquids which either have a very low vapor pressure or which can be cooled without solidification to temperatures where their vapor pressure is negligible.

Due to its low melting point, n-octene is a compound especially suitable for investigating plasma–liquid interactions. Its oxidation to the corresponding epoxide and aldehyde has been studied both with plasmas of pure oxygen[2] and mixtures of oxygen with inert gases.[3]

Many olefins have a vapor pressure too high for a plasma treatment of this kind even near their melting point. It was of interest to study the possibility of treating such compounds in solutions of low-melting solvents.[4] If this technique were applicable, it would greatly increase the number of suitable starting materials. Some preliminary experiments on plasma reaction in solution have been reported by Mazur.[5]

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2. SELECTION OF SOLVENTS

A solvent for the oxidation of olefins should be low-melting, inert against oxygen plasmas, and completely miscible with the starting material. There is no solvent which totally fulfills all these requirements. The perfluorocarbons, which are inert against oxygen plasmas, are very poor solvents for the olefins. All other solvents are attacked by oxygen plasmas. As a compromise, it seems possible to use solvents which react with oxygen plasmas sufficiently more slowly than the alkenes. We selected three cycloalkanes and an ether, all of which have physical properties similar to those of n-octene:

	mp (°C)	bp (°C)	p (Pa) extrapolated to −95°C
Dimethylbutane	−128.5	58	$\approx 1.5 \times 10^{-5}$
1,4-Dimethylcyclohexane	−87.4	124.2	2.6×10^{-7}
Etylcyclohexane	−111.3	131.8	1.4×10^{-7}
Dibutyl ether	−98	142	1.1×10^{-7}
1-Octene	−101.7	121.3	1.5×10^{-7}

Extrapolation of reported vapor pressures ($10g\ p$ versus $1/T$) to the range of investigations ($-95°C$) shows only the vapor pressure of dimethylbutane to be considerably higher than that of octene while those of the other solvents are almost identical.
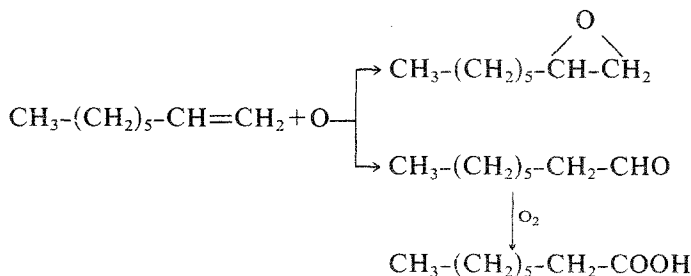
3. EXPERIMENTAL

In the experimental setup, which has been described previously,[3,4] liquids were stirred magnetically and cooled in a bath of methanol to −93 to −97°C. A flow of oxygen of 2.5 liters/h passed the plasma generated by a 13.56-MHz generator, matching network, and a copper coil surrounding a glass tube which ended a few millimeters above the surface of the liquid. The distance between the latter and the lower end of the inductive coil was 15 cm. The power was monitored by a Thruline wattmeter. Each mixture was treated for 15 min at a power level of 100 W.

n-octene (EGA 99%), ethylcyclohexane (Merck 98%), 1,4-($cis/trans$)-dimethylcyclohexane (EGA 99%), 2,3-dimethylbutane (EGA 98%), and dibutyl ether (Janssen 99%) were used without further purification. Products were identified by GC (HP 5750 and P.E. F20H) using columns of 2–5 m with 10% OV 17 and 10% Carbowax respectively on Chromosorb W 60/80 for the liquid products, and 2m GSC–120 Al_2O_3 or Poropak S for the gases condensed in LN2 traps. Correction factors for the individual compounds were applied. For quantitative determinations the liquids were weighed and the amount of gases determined by the pressure increase on warming of the cool trap.

4. RESULTS

When mixtures of octene and 2,3-dimethylbutane were exposed to an oxygen plasma at about $-95°C$ no liquid oxidation products but only carbon dioxide (70–80%) and several low-molecular-weight hydrocarbons were found. The yields and the product distribution did not change when the solvent fraction was varied between 4 and 100%. In contrast to this, mixtures of octene and 1,4-dimethylcyclohexane yielded hardly any gases. The liquid oxidation products were the same as in the treatment of neat octene,[2,3] with 1-octene epoxide being the major constituent, and octanal and octanoic acid the minor constituents:

$$CH_3\text{-}(CH_2)_5\text{-}CH{=}CH_2 + O \left[\begin{array}{l} \rightarrow CH_3\text{-}(CH_2)_5\text{-}\overset{\displaystyle O}{\overset{\diagup\ \diagdown}{CH\text{-}CH_2}} \\[2em] \rightarrow CH_3\text{-}(CH_2)_5\text{-}CH_2\text{-}CHO \\ \qquad\qquad\qquad\quad \downarrow O_2 \\ CH_3\text{-}(CH_2)_5\text{-}CH_2\text{-}COOH \end{array}\right.$$

At 100 W and a reaction time of 15 min alkene conversion was 20–40% increasing slightly with dilution by the solvent (Table I). While absolute yields decreased slightly with dilution, normalized yields (yield/% octene) pass through a maximum at $\approx 70\%$ solvent. The data show considerable scatter, probably due to the high viscosity of these mixtures at $-95°C$. The ratio epoxide/aldehyde forming reactions remained constant over the entire range. Only in mixtures with the highest solvent content were a few percent of 1,4-dimethylcyclohexanol found. Neat 1,4-dimethylcyclohexane at $-95°C$ is a solid and yields only carbon dioxide:

$$H_3C\text{-}\langle\ \rangle\text{-}CH_3 + O \longrightarrow \overset{H_3C}{\underset{HO}{>}}\langle\ \rangle\text{-}CH_3$$
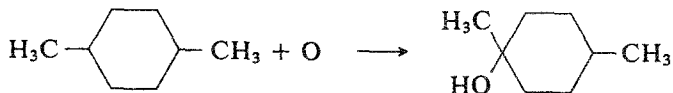
Similar results were found for combinations of octene and ethylcyclohexane, with the epoxide, aldehyde, and acid accounting for 82–94% of the products in all cases (Table I). In contrast to the results mentioned above, on dilution with ethylcyclohexane/octene the absolute yields were nearly constant up to 80% solvent addition, while the normalized yields increased strongly with dilution. The ratio epoxide/aldehyde remained 1.4 up to 70% ethylcyclohexane but increased to 1.9 at higher dilutions. In mixtures containing $> 80\%$ solvent small quantities ($\leq 2\%$) of ethylhexanol were found.

Table I. Oxidation of n-Octene in the Presence of Solvents (Normalization: Absolute Yields/Fraction Octene in Mixture)

Solvent addition (%)	Octene conversion (%)	Epoxide among products (%)	Liquid products	
			Average yields[a] absolute (mmol/kWh)	Average yields[a] normalized (mmol/kWh)
		1,4-Dimethylcyclohexane		
0	20 ± 3	28 ± 6	349 ± 55	349 ± 55
10	23 ± 2	38 ± 5	364 ± 20	405 ± 22
20	19 ± 1	31 ± 8	269 ± 20	337 ± 25
30	16 ± 2	35 ± 4	204 ± 30	292 ± 42
40	35 ± 6	39 ± 5	394 ± 50	657 ± 84
50	32 ± 5	39 ± 8	287 ± 47	574 ± 94
60	37 ± 3	34 ± 4	280 ± 34	701 ± 85
70	49 ± 7	34 ± 3	263 ± 38	875 ± 125
80	43 ± 2	21 ± 2	154 ± 4	772 ± 19
90	38 ± 8	23 ± 2	68 ± 15	677 ± 147
		Ethylcyclohexane		
10	20 ± 2	35 ± 7	318 ± 22	353 ± 25
20	27 ± 4	46 ± 2	382 ± 56	477 ± 70
30	30 ± 1	40 ± 8	382 ± 7	546 ± 10
40	38 ± 2	41 ± 5	406 ± 17	677 ± 29
50	47 ± 4	43 ± 6	417 ± 35	835 ± 70
60	49 ± 5	41 ± 2	350 ± 37	875 ± 92
70	65 ± 9	44 ± 3	348 ± 51	1161 ± 171
80	96 ± 1	49 ± 1	344 ± 3	1719 ± 13
90	96 ± 1	57 ± 6	172 ± 1	1715 ± 14
		Dibutyl ether		
10	24 ± 3	50 ± 7	390 ± 55	433 ± 61
20	32 ± 2	53 ± 2	459 ± 25	574 ± 30
26	32 ± 6	54 ± 2	420 ± 69	568 ± 94
36	37 ± 2	52 ± 3	418 ± 24	653 ± 38
46	48 ± 5	48 ± 5	463 ± 42	858 ± 78
56	53 ± 4	57 ± 8	415 ± 34	942 ± 76
66	66 ± 4	47 ± 7	399 ± 22	1174 ± 63
78	90 ± 3	55 ± 5	352 ± 10	1602 ± 45
88	86 ± 4	53 ± 14	185 ± 10	1546 ± 80

[a] Averages of three to four individual runs.

Mixtures of octene and dibutyl ether yielded the same products as neat octene; however, the amount of acid formed was lower ($\leq 5\%$). The ratio epoxide/aldehyde was independent of the composition of the liquid. Above 66% dibutyl ether some oxidation products of the dibutyl ether were observed. The absolute yields increased with dilution, reaching a maximum

at 50% solvent addition and remaining high up to 80% solvent (Table I). Normalized yields strongly increased with dilution.

5. COMPARISON OF THE SOLVENTS

In spite of their similar physical properties, the four solvents influence the oxidation of octene quite differently. A dilution with dimethylbutane completely prevents the oxidation of octene; dimethylcyclohexane causes somewhat lower yields; but ethylcyclohexane and dibutyl ether give better results than neat octene. In experiments with dimethylcyclohexane there are traces of low-molecular-weight products, indicating competing gas-phase reactions. The viscosity of the mixtures has not been determined, but due to its melting point of $-87.4°C$ dimethylcyclohexane mixtures at $-95°C$ probably have a higher viscosity than those of the other solvents. The amount of liquid products is highest in dibutyl ether, slightly lower in ethylcyclohexane, and still somewhat lower in dimethylcyclohexane (Fig. 1).

As illustrated in Fig. 1, addition of dibutyl ether or ethylcyclohexane up to 80% hardly affects the octene oxidation. It might be of considerable interest, for synthetic work, that the absolute yields increase by $\approx 30\%$ on addition of $\approx 50\%$ solvent. Furthermore there is a significant increase in the percentage of epoxide among the products (Table II).

Table II represents the averages of about 30 individual runs for each solvent system at constant reaction times and power, but with varying
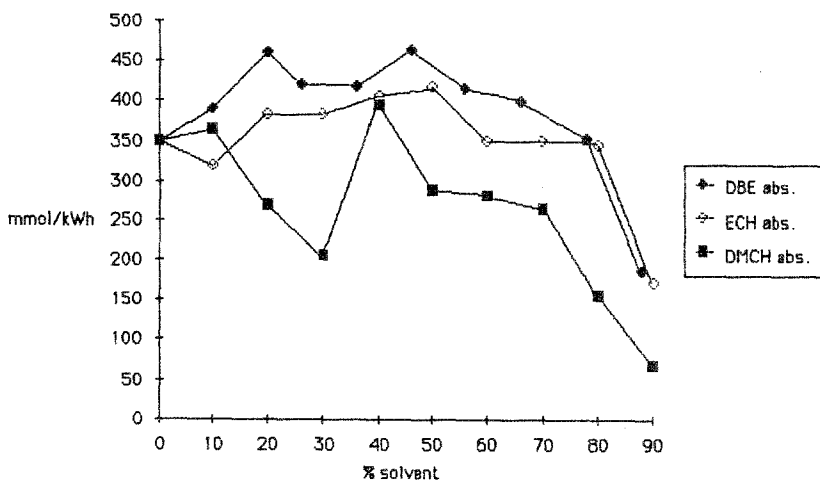

Fig. 1. Yields of liquid products obtained from mixtures of octene with dibutyl ether (DBE), ethylcyclohexane (ECH), and dimethylcyclohexane (DMCH). Experiments at $-95°C$, 100 W, 15 min.

Table II. Comparison of Yields and Products Obtained in n-Octene Oxidation in the Presence of Solvents (E = Octene Epoxide, A = Octanal, S = Octanoic Acid)

	Octene conversion (%)	E + A + S products (%)	E/A	E/A+S	A/S	Epoxide (mmol/kWh)
Dimethylcyclohexane	31.8	75	1.40	0.90	1.62	114 ± 31^{a}
Ethylcyclohexane	49.9	94	1.43	1.04	2.92	159 ± 33^{a}
Dibutyl ether	48.4	88	1.56	1.30	5.21	228 ± 21^{a}
Neat Octene	19.6	75	1.36	0.63	0.85	100 ± 15

^{a} At 50% solvent addition.

fractions of the solvent. Of the three systems, ethylcyclohexane causes the least amount of by-products, and dimethylcyclohexane the highest. For synthetic work, dibutyl ether is the best choice, giving the highest yields of the epoxide (Fig. 2).

6. ADDITION OF CF$_4$

When the oxidation of octene was carried out using mixtures of oxygen and helium or nitrogen, the yields were up to four times those of neat oxygen.[3] It was of interest to study the effect of tetrafluoromethane, an
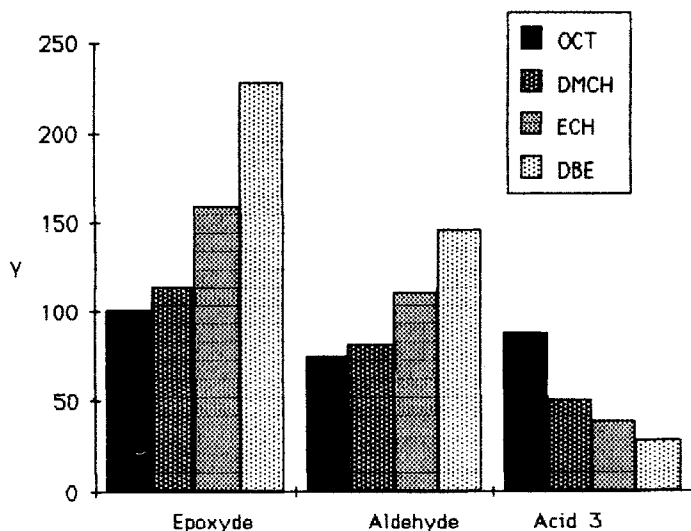

Fig. 2. Distribution of the main products in neat octene (OCT) and octene diluted by 50% solvent (DMCH = 1,4-dimethylcyclohexane, ECH = ethylcyclohexane, DBE = dibutyl ether).
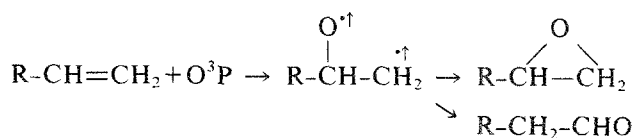
additive known to improve oxygen attack in etching. When neat octene was oxidized by mixtures of oxygen and tetrafluoromethane, yields and product distributions changed drastically. Addition of 1 and 6% CF_4 reduced the yields to 50 and 25% respectively. Addition of $\geq 20\%$ CF_4 completely eliminated the epoxide formation. A 33–70% CF_4 addition caused the formation of various liquid fluoro compounds; above 70% CF_4 addition no liquid products were observed. In contrast to this, 0.1–10% addition of CF_4 causes a 100% increase in yields in the oxidation of neat ethylcyclohexane. In the latter case, reactions start by hydrogen abstraction, a process which is much faster in the presence of fluorine atoms. In the reaction with olefins, fluorine atoms cannot help the addition of oxygen atoms. Because of their capability to capture electrons, fluorine atoms and fluorine compounds cause a decrease in free electrons and thus a reduction in yields.

7. DISCUSSION

The experiments demonstrate the possibility of using solvents in the plasma oxidation of liquid octene. Plasma reactions with solutions of other species are probably also possible. The use of solvents seems, however, to be restricted to compounds which have a lower or similar vapor pressure as the substance to be oxidized. If it is higher, no reaction with the substrate occurs. It seems likely that the vapor of the solvent prevents attacking species from reaching the surface.

The main constituents of oxygen plasmas are ground-state molecules $X^3\Sigma^-$, singlet oxygen molecules $^1\Delta_g$, and ground-state oxygen atoms ^3P. Ozone can be neglected in the low-pressure range. Singlet oxygen may react with allylic hydrogens to form hydroperoxides; toward other hydrogens, it is inert.[6-9] Oxygen atoms can add to olefinic double bonds or abstract hydrogen atoms from C–H bonds.[10]

The products formed from octene indicate oxygen atoms to be the only attacking species. Hydroperoxides have never been detected even in freshly prepared product mixtures. The reaction of oxygen atoms ^3P with double bonds leads to a biradical,[10-12] which can stabilize either by cyclization to form the epoxide or by isomerization to form the aldehyde:

$$R\text{-CH}=\text{CH}_2 + O^3P \rightarrow R\text{-}\overset{\overset{\displaystyle O^{\cdot\uparrow}}{|}}{\text{CH}}\text{-}\overset{\cdot\uparrow}{\text{CH}}_2 \rightarrow \overset{\overset{\displaystyle O}{\diagup\ \diagdown}}{R\text{-CH}\text{-CH}_2}$$
$$\searrow R\text{-CH}_2\text{-CHO}$$

The relative importance of the two routes is influenced by the solvent. As compared to the gas phase, all liquids favor the cyclization, probably because they can quench the hot cyclization product more efficiently. There must,

however, be a further specific solvent effect since the ratio epoxide/aldehyde is significantly higher in dibutyl ether and ethylcyclohexane than in neat octene.

ACKNOWLEDGMENT

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