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The influence of volatile organic compound structure on conditions required for total oxidation

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Abstract

The reactivity of a range of volatile organic compounds with differing functional groups has been assessed over platinum catalysts supported on β-zeolite, mordenite, silica or alumina. Alcohols, ketones, carboxylic acids, aromatics and alkanes were included in the range. In general, the reactivity pattern observed was alcohols > aromatics > ketones > carboxylic acids > alkanes, although some overlap was observed in that the more reactive alkanes were more readily oxidized than the less reactive carboxylic acids. The same order of reactivity was observed for all the catalysts studied here. A kinetic isotope effect was observed when deuterated acetone was compared to normal acetone, consistent with C–H bond cleavage being the slow step in the catalytic oxidation of this substrate. A correlation was found between the reactivity of the individual substrates and the strength of the weakest C–H bond in the structure. A single weak C–H bond in the substrate led to a high reactivity. It is postulated that catalytic oxidation on platinum catalysts proceeds via initial rupture of the weakest C–H bond in the substrate followed by further reaction steps which involves free radical chemistry. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds (VOCs) are an important class of air pollutants, commonly found in the atmosphere at ground level in all urban and industrial centres. A working definition would include any carbon-containing compound present in the atmosphere, excluding elemental carbon, carbon monoxide and carbon dioxide [1]. Approximately 235 millions tonnes of VOCs are released per year into the atmosphere by man-made sources. Global emissions of natural hydrocarbons are estimated at 830–2100 million tonnes per year [2]. European emissions of low molecular-mass volatile organic compounds from human activities amounts to about 24 million tonnes per year, similar in size to sulphur dioxide and nitrogen dioxide emissions, each of the order of 20 million tonnes per year [3]. The three major sources of VOCs are: power generation (20%), vehicle emissions (40%) and solvents (27%) [4].

VOCs tend to be present in outdoor air at the level of the parts per billion, and in indoor air at the level of parts per million. Typical examples for indoor air include:

styrene from insulation, textiles, paints, disinfectants and plastics; alcohols from aerosols, window cleaners, paints and cosmetics;
ketones from lacquers, varnishes and adhesives; ethers from resins and paints;
terpenes from polishes, fabrics, fabric softeners, cigarettes and food;

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aromatic hydrocarbons from paints, adhesives, gasoline and combustion products;
benzene from tobacco smoke; and
carbon tetrachloride from industrial cleaners [5].

A technology for the treatment of very low concentrations of a diverse number of VOCs in indoor air through catalytic oxidation, in conditions which require very low energy input, is actively being sought.

A large number of studies of the oxidation of VOCs on heterogeneous catalysis simply report phenomenological data relating to the conditions of catalysts composition, temperature and flow rate required for the destruction of a single VOC. Other studies report on the behaviour of mixtures of VOCs. In view of the complex nature of any mixture of VOCs and the differing reactivities derived from their differing chemical structures, it is important to develop an understanding of the factors which determine VOC reactivity over oxidation catalysts.

Yao [6] studied the reactivity of C1–C4 alkanes over typical Pt/Al_2O_3 and Pd/Al_2O_3 combustion catalysts. Reaction commenced at about 250°C, and a 100% conversion of each alkane was possible close to 500°C. A clear order of destructibility emerged with butane being the easiest to oxidize and methane the hardest.

Several workers have looked for the reasons behind the differing reactivities of different substrates. Sokolovskii [7] shows a correlation between the rate of oxidation of *n*-alkanes on cuprous oxide and the bond dissociation enthlapy of the weakest C–H bond in the alkane. This work indicates that the weaker the C–H bond strength in an *n*-alkane, the more readily it is oxidized over the cuprous oxide catalyst.

Schwartz et al. [8] used a wider range of substrates, including alkanes, alkenes, alcohols and ketones and concluded that, over platinum or palladium catalysts, the reactivity of a substrate towards oxidation was related to the bond energy of the weakest bond in the substrate, although no bond energy data was presented in this study. This led to a proposal on the mechanism whereby the substrate was activated on the metal surface through rupture of the weakest C–H bond. The species which formed then reacted rapidly with surface oxygen species to yield total oxidation products.

In studies by Palazzolo and Tichenor [9], and later by Hermia and Vigneron [10] — each working with a range of substrates with differing functional groups — the following order of reactivity was established:

$$\text{alcohols} > \text{aldehydes} > \text{aromatics} > \text{ketones} > \text{alkenes} > \text{alkanes}$$

This work concentrates on the factors which determine the reactivity of a wide range of VOCs, including, alcohols, aromatics, ketones, carboxylic acids and alkanes, over a range of platinum catalysts supported on zeolites and conventional supports, with a view to determining if there are generic factors inherent in the structure of these VOCs which determine reactivity A second objective was to determine whether reactivity sequences are dependent on the structure of the catalyst and a third objective was to establish for a wide range of VOCs present at concentrations typically encountered in contaminated indoor air, the minimum temperatures (hence minimum energy input) required over an active catalyst to achieve destruction of the VOCs.

2. Experimental

For the experiment, 2.1 wt.% Pt/Al_2O_3 and 2 wt.% Pt/SiO_2 were prepared by wet impregnation using a solution of H_2PtCl_6. 0.5 wt.% Pt/β-zeolite, and 0.34 wt.% Pt/mordenite were prepared by ion exchange with $Pt(NH_3)_4{}^{2+}$. Further details have been given elsewhere [11]. All catalysts were dried, calcined and reduced in hydrogen flow. The platinum contents were measured by atomic absorption spectroscopy. Other characterization included measurement of the BET surface areas by nitrogen adsorption and metal dispersion by hydrogen chemisorption.

The performance of 2.1 wt.% Pt/Al_2O_3, 2 wt.% Pt/SiO_2, 0.5 wt.% Pt/β-zeolite, and 0.34 wt.% Pt/mordenite were investigated for the complete oxidation of a wide variety of VOCs; ethanol, 1-propanol, 2-propanol, ethylbenzene, toluene, acetone, deuterated acetone, acetic acid, methane, ethane, propane and *n*-butane. The source of each alkane was a cylinder which contained 1.03% methane in helium, 1.01% ethane in helium, 0.95% *n*-butane in helium or 0.96% propane in helium. All other VOCs were generated by passing a part of the helium stream through a saturator, which contained a molecular sieve saturated with the VOC, held at 0°C. The appropriate partial pressure of VOC was generated by adjusting the fraction of the total helium flow that was passed through

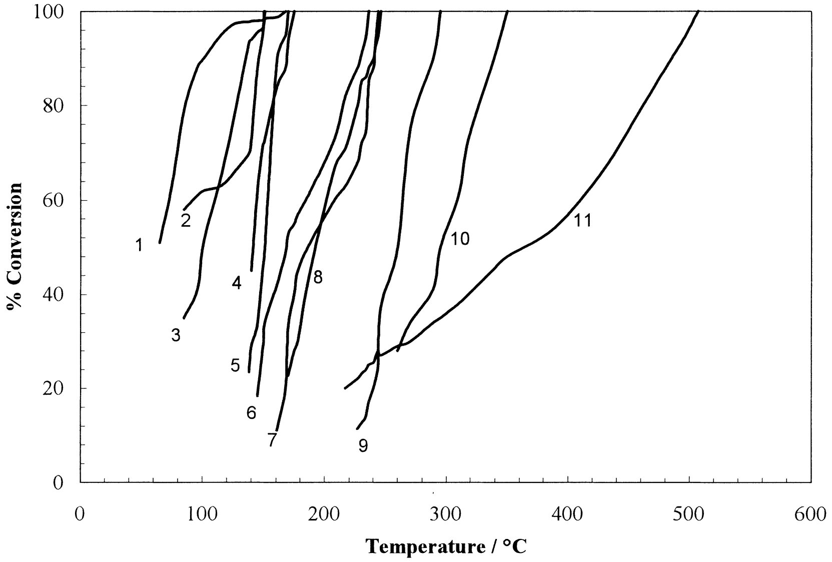

Fig. 1. Destructibility of the indicated hydrocarbons over 0.5 wt.% Pt/β -zeolite (P_{VOC} = 1000 ppm, P_{Oxygen} = 12 vol%, W/F = 0.12 g s/ml). 1, 1-Propanol; 2, 2-propanol; 3, ethanol; 4, toluene; 5, ethylbenzene; 6, acetone; 7, butane;, 8, propane; 9, acetic acid; 10, ethane; 11, methane.

the saturator. For the oxidation of each VOC, the feed stream through the reactor contained 12 vol.% oxygen, 0.1 vol.% VOC, and the remainder being helium.

In all the experiments, 0.1 g catalyst, in the form of a fine powder, was tested using a quartz glass vertical reactor tube. The catalyst was held in position by two plugs of quartz wool. The feed stream entered a series of three-way valves which allowed the reactor to be bypassed, or not, as required. A K type thermocouple was inserted directly into the catalyst bed. The temperature of the furnace was controlled by a Eurotherm. Before testing, the catalyst was pre-treated for 90 min in a stream of helium or hydrogen at 30 ml/min at 400°C. After pre-treatment, the catalyst was cooled to the desired temperature and the reaction was started by introducing the reactant stream. The effect of temperature on the catalytic oxidation of these VOCs was examined, by increasing the reaction temperature, from 50 to 500°C at regular intervals. Steady-state activities were measured at each temperature. Product gases were analyzed by on-line gas chromatography (Varian model 3400 GC) using a Porapak T column and a thermal conductivity detector.

Table 1
Characterization of supported platinum catalysts

Catalyst	BET surface area (m^2/g)	Pt dispersion (%)
0.5%Pt/Beta	554	38
0.34%Pt/mordenite	273	57
2.1%Pt/Al_2O_3	96	86
2% Pt/SiO_2	55	28

3. Results and discussion

Basic characterization data for the catalysts used in this study are presented in Table 1 and point to a wide variation in carrier characteristics and metal dispersions. The destructibility through oxidation of the full range of VOCs studied over 0.5%Pt/Beta and 2%Pt/SiO_2 is summarized in Figs. 1 and 2, respectively. A clear order in destructibility was observed whereby alcohols are most readily oxidized, followed by the aromatics, then acetone and the alkanes. Within the alkanes, methane is the most difficult to oxidize followed by ethane, propane and *n*-butane. Acetic acid is more difficult to oxidize than the *n*-butane or propane. A further compilation of these data, presented in terms of the temperatures required for 50% and 100% destruction of the VOCs on all four catalysts used here is presented in Table 2. A point to note is that the same destructibility order can be noted for all the catalysts used, but that the exact conditions required to achieve

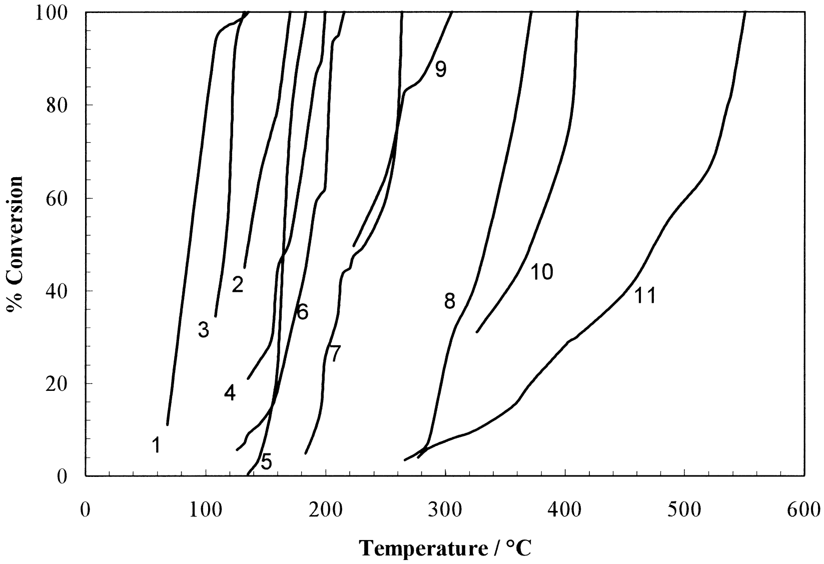

Fig. 2. Destructibility of hydrocarbons over 2 wt.% Pt/SiO$_2$ ($P_{\mathrm{VOC}}=1000$ ppm, $P_{\mathrm{Oxygen}}=12$ vol%, W/F = 0.12 g s/ml). 1, 1-Propanol; 2, 2-propanol; 3, ethanol; 4, toluene; 5, ethylbenzene; 6, acetone; 7, butane;, 8, propane; 9, acetic acid; 10, ethane; 11, methane.

Table 2
Temperatures (°C) required for 50% and 100% conversion of the indicated substrates over supported platinum catalysts

	0.5%Pt/Beta		0.34%Pt/mordenite		2% Pt/SiO$_2$		2.1%Pt/Al$_2$O$_3$	
	T_{50}	T_{100}	T_{50}	T_{100}	T_{50}	T_{100}	T_{50}	T_{100}
Ethanol	101	132	80	126	135	165	118	161
1-Propanol	65	168	90	155	85	135	151	185
2-Propanol	51	159	83	149	80	129	146	173
Toluene	142	175	174	197	170	200	228	240
Ethylbenzene	151	170	172	205	150	183	205	223
Acetone	170	220	165	220	196	236	200	245
Acetic Acid	265	295	219	259	271	305	276	308
n-Butane	230	244	230	260	233	263	368	450
Propane	195	246	239	265	330	371	398	461
Ethane	295	350	275	345	371	410	410	490
Methane	389	507	356	441	461	550	486	512

a specified level of destruction through oxidation does depend on the catalyst composition.

No products of selective oxidation were observed in any of this work except with the alcohols, where the corresponding carboxylic acids were detected. This is illustrated in Fig. 3 for the oxidation of ethanol over 0.5% Pt/Beta. Considerable amounts of acetic acid were detected even in conditions where ethanol conversion had exceeded 100%. A point to note, therefore, is that the data presented previously (in Figs. 1 and 2 and in Table 2) concerning alcohol destruction refer strictly to the conditions required for the consumption of the alcohols and does not refer to its complete destruction to carbon dioxide and water.

Fig. 4 compares the reactivity of acetone and deuterated acetone over 0.5% Pt/Beta. The data indicate that, when conversion exceeded 10%, the deuterated material was considerably less reactive. Specifically for

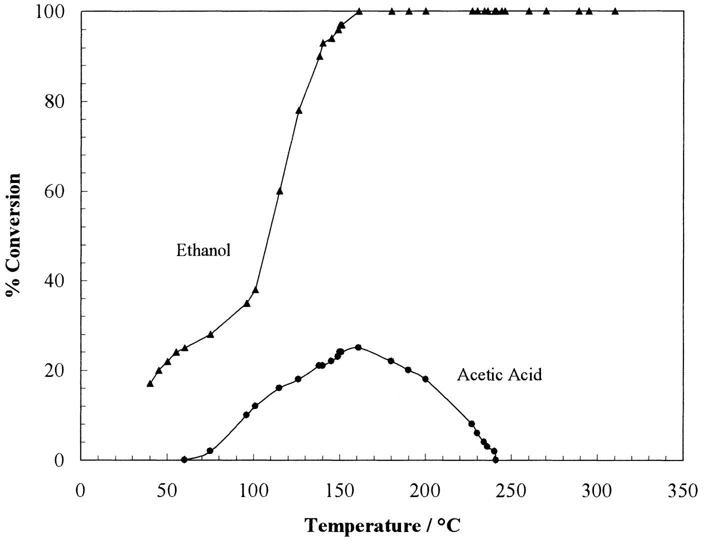

Fig. 3. Oxidation of ethanol over 0.5 wt.% Pt/Beta. ($P_{ethanol}$ = 1000 ppm, P_{oxygen} = 12 vol%, W/F = 0.12 g s/ml).

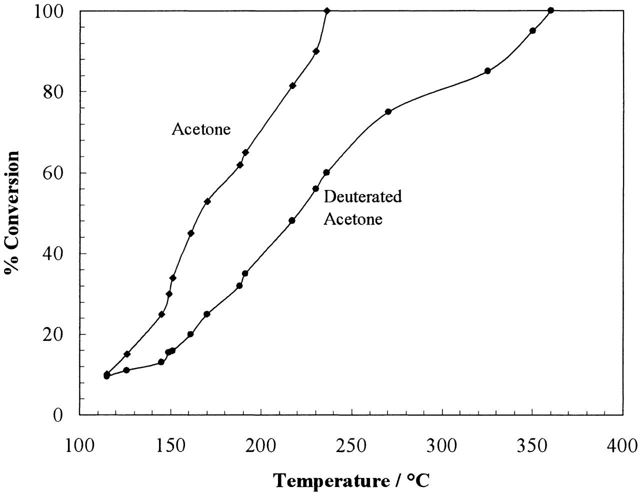

Fig. 4. Catalytic oxidation of acetone and deuterated acetone over 0.5 wt.% Pt/Beta. (P_{VOC} = 1000 ppm, P_{oxygen} = 12 vol.%, W/F = 0.12 g s/ml).

170°C, the experimentally measured $k_H : k_D$ ratio was 2.5 against a theoretically predicted value of 3.1 [12]. Similar data were recorded for all the catalysts studied here and are consistent with a slow step in the reaction mechanism in which a C–H bond is almost fully cleaved.

In order to investigate whether cleavage of C–H bonds is generally important for the full variety of substrates studied here, a table of bond dissociation enthalpies (Table 3) was prepared [13]. In this table, the weakest bond in each substrate is indicated. Figs. 5 and 6 present the relationship between T_{50} and T_{100} (the temperatures required for 50% and 100% destruction of a given VOC) recorded over 0.5% Pt/Beta for each substrate and the bond dissociation enthalpy of the weakest C–H bond in that substrate. A similar

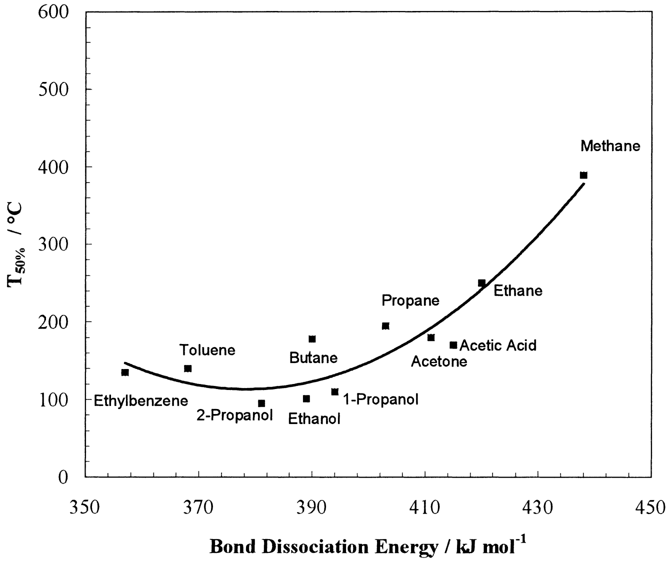

Fig. 5. Relationship between bond dissociation energy (kJ/mol) of the weakest substrate C–H bond and the temperature required for 50% conversion of the corresponding VOC. (P_{VOC} = 1000 ppm, P_{oxygen} = 12 vol%, W/F = 0.12 g s/ml, catalyst = 0.5 wt.% Pt/Beta).

Table 3
Table of C–H bond dissociation enthalpies [13]

Compound	Bond dissociation enthalpies (kJ/mol)
CH_4	438
CH_3CH_3	420
$CH_3\underline{CH}_2CH_3$	401
$CH_3CH_2\underline{CH}_2CH_3$	390
$C_6H_5\underline{CH}_2CH_3$	357
$C_6H_5\underline{CH}_3$	368
$CH_3\underline{CH}_2OH$	389
$C_2H_5\underline{CH}_2OH$	394
$CH_3\underline{CH}OHCH_3$	381
$\underline{CH}_3COCH_3$	411
$\underline{CH}_3COOH$	415

trend was observed for all conversion levels between 10 and 100%, and the same sequence of destructability was observed for all four catalysts studied here. Clearly, a correlation is observed between these factors and, in general, we can conclude that the strength of the weakest C–H bond in the substrate is an important factor in determining reactivity consistent with the earlier works of Sokolovskii [7] and Schwartz et al. [8]. Strictly speaking, the correlations shown in Figs. 5 and 6 refer to the temperatures required for the first step in the total oxidation of the VOC. This is clearly the case for the alcohols used in this study, since they were oxidized to carboxylic acids, which corresponds to a kinetically more stable compound than the parent alcohol. With all other VOCs studied, no products of partial oxidation were observed and in these cases no partial oxidation product is released into the gas phase that is less reactive than the parent VOC.

Other factors may, however, also contribute to the correlations observed in Figs. 5 and 6, especially in view of the reasonably low temperatures at which, for example, alcohol oxidation to carboxylic acid occurs with these catalysts (see Figs. 1 and 2). In doing this work, alcohols were the only class of VOCs which adsorbed extensively onto the catalysts at temperatures just below those required for reaction. It is likely that, even at the reaction onset temperature, the reactive surface was covered by adsorbed alcohol, probably in the form of adsorbed alkoxides which, subsequently, reacted to initially form carboxylic acid products and, finally, products of total oxidation. The extensive adsorption of the alcohols on these catalysts may explain why the alcohols, with somewhat stronger C–H bonds than the aromatics (see Table 3), nevertheless, require slightly lower temperatures to achieve the same levels of conversion.

Notwithstanding these observations, bond dissociation enthalpies remain a key parameter in determining

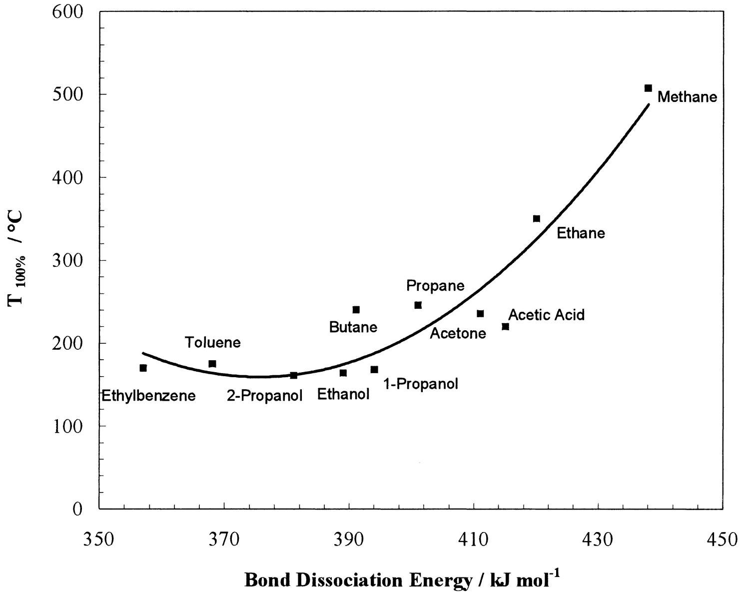

Fig. 6. Relationship between bond dissociation energy (kJ/mol) of the weakest substrate C–H bond and the temperature required for 100% conversion of the corresponding VOC ($P_{\mathrm{VOC}} = 1000$ ppm, $P_{\mathrm{oxygen}} = 12$ vol%, W/F = 0.12 g s/ml, catalyst = 0.5 wt.% Pt/Beta).

reactivity of substrates and the data presented here are consistent with a reaction mechanism whereby the slow step is cleavage — with the aid of the catalyst surface — of the weakest C–H bond in the substrate. A key point in this argument is that active sites on these surfaces activate VOCs preferentially at C–H. After this initial activation, free radical species may form according to:

$$\mathrm{RH} \rightarrow \mathrm{R}^{\bullet} + \mathrm{H}^{\bullet}$$

The energetics of these species may be moderated somewhat by surface interactions, but the essential fact is that they should be sufficiently energetic to react with any source of oxygen, adsorbed or gas phase, available in the reactor, leading to the formation of total oxidation products.

In certain circumstances, products of partial oxidation may escape into the gas phase and, if their inherent reactivity is less than that of the parent VOC, higher temperatures will be required to achieve total oxidation. Such is the case in the oxidation of alcohols with the formation of carboxylic acids. In this situation, the carboxylic acid represents a kinetic trap because all the C–H bonds in the carboxylic acid are stronger than the weakest C–H bond in the parent alcohol [14].

4. Conclusions

A primary factor in determining the reactivity of volatile organic compounds in oxidation reaction is the strength of the weakest C–H bond in the structure. Compounds with a single weak C–H bond are more readily destroyed by oxidation on a supported platinum catalyst. Other factors, such as adsorption, may also become important, especially in circumstances where the volatile organic compound reacts at a very low temperature. The mechanistic implication of this work is that destruction of volatile organic compounds over oxidation catalysts proceeds by initial rupture of the weakest C–H bond in the compound, followed by further steps that may involve free radical chemistry.

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