Evidence for Surface Activation in the Photolysis of Adsorbed Lead Tetraethyl

By D. L. Perry and M. W. Roberts*
(*School of Chemistry, University of Bradford,* BD9 1DP)

Summary Condensed multilayers of $PbEt_4$ decompose when irradiated with u.v. light of wavelength 254 nm to give gaseous C_2 and C_4 hydrocarbons and a lead film; adsorbing $PbEt_4$ on a photodeposit of Pb generates a more reactive species which is active in photolysis at longer wavelengths (280—290 nm).

We report a study of the photolysis of adsorbed multilayers of $PbEt_4$ undertaken to determine the mechanism of surface photolysis and its contribution to the overall process of lead deposition from $PbEt_4$ vapour.[1] The surface photolysis was followed by monitoring the increase in gas-phase pressure, the nature of the gaseous products being determined either by g.l.c. or by an omegatron mass-spectrometer attached to the glass reaction vessel. The latter was designed so that $PbEt_4$ could be adsorbed on a glass surface cooled to *ca.* 273 K by circulating an ice–water mixture; u.v. light was incident on this surface *via* a quartz window. The vapour pressure of $PbEt_4$ is sufficiently low (*ca.* 5×10^{-2} Torr) at 273 K to ensure that gas-phase photolysis is negligible; further, no photodeposits are formed on the quartz window which would reduce the light intensity. Two light sources were used (i) a 15 W Philips low-pressure Hg lamp which, in conjunction with a Corning glass filter, gave a *monochromatic* source of wavelength 254 nm. (ii) a 250 W high-pressure Hg lamp emitting one band of u.v. radiation from 240 and 260 nm and a second broad band from 280 nm to > 340 nm. The intensity maxima in the two bands were at 250 and 315 nm. The light from both lamps was focussed by means of a spectrosil lens to a spot ($0{\cdot}2$ cm^2 area) on the cooled glass surface.

The rate of photolytic decomposition of $PbEt_4$ adsorbed on glass at 273 K using 254 nm radiation was constant at $4{\cdot}5 \times 10^{15}$ molecules min^{-1} of gaseous hydrocarbon products and independent of surface concentration in the range 2×10^{17}—15×10^{17} molecules cm^{-2} (10^3—$7{\cdot}5 \times 10^3$ monolayers of $PbEt_4$). The ratio of C_2 to C_4 hydrocarbons in the products was $3{\cdot}6:1$ and the quantum yield of the photolysis was $0{\cdot}04$. The rate was shown to be directly proportional to the light intensity, independent of the pressure of added N_2(g), and not affected by adsorbing $PbEt_4$ on a photodeposit of lead rather than on a glass surface.

The extinction coefficient[2] of $PbEt_4$ at 254 nm is high (2×10^3 l mol^{-1} cm^{-1}) and more than 90% of the light was shown to be absorbed by surface concentrations of $PbEt_4$ greater than 2×10^{17} molecules cm^{-2}. That the surface photolytic reaction occurs at a constant rate which is independent of the nature of the adsorbent–adsorbate interface is therefore understood in terms of the adsorption characteristics of $PbEt_4$.

When the photolytic reaction was investigated with the high-pressure lamp, the rate at 273 K was $2{\cdot}5 \times 10^{16}$ product molecules min^{-1} and independent of both added N_2(g), and the surface concentration of $PbEt_4$. The rate was directly proportional to the light intensity. However, there was an important difference from the studies with the low-pressure lamp in that the surface on which the $PbEt_4$ was adsorbed had a marked influence on the rate of photolysis. In particular when $PbEt_4$ was condensed on a Pb photodeposit, formed in a previous experiment, the rate of photolysis was *ca.* 3 times faster than for $PbEt_4$ adsorbed on a 'clean' glass surface. This was not the case using monochromatic radiation of 254 nm. Analysis of the gaseous products (a mixture of butane, ethane, and ethylene) indicated a C_2–C_4 ratio of $1{\cdot}4$—$1{\cdot}5:1$ (*cf.* $3{\cdot}6:1$ with the low pressure lamp) which was independent of the nature of the underlying surface. The introduction of a Pyrex filter which absorbed wavelengths shorter than *ca.* 290 nm stopped the photolysis.

At 290 nm the extinction coefficient of $PbEt_4$(g) is low (25 l mol^{-1}); more than 90% of this light wavelength is calculated to be transmitted by the condensed phase $PbEt_4$(c) and is therefore incident on the adsorbent–adsorbate interface. Since the light of wavelengths around 254 nm has been shown to be completely adsorbed by the physically adsorbed $PbEt_4$, the increase in the rate of photolysis observed with the high pressure lamp when $PbEt_4$ is adsorbed on a lead surface must be due to light of longer wavelengths inducing a photolytic reaction at the Pb–$PbEt_4$ interface. The use of filters narrows the active wavelengths to the range 280—290 nm.

We therefore suggest that surface species formed by adsorbing $PbEt_4$ on a Pb substrate at 273 K are activated, in the sense that they are decomposed at longer wavelengths than the unperturbed $PbEt_4$ molecule in the condensed phase. There are therefore two simultaneous processes (a) photolysis of the condensed phase $PbEt_4$(c) by $\lambda = ca.$ 254 nm and (b) surface photolysis at the Pb–$PbEt_4$(c) interface by light of $\lambda = ca.$ 280 nm. We suggest that the gaseous hydrocarbons are formed as in reactions (1)—(5) (c = condensed phase; g = gaseous phase).

$$\mathrm{Pb(Et)_1(c)} + h\nu \longrightarrow \mathrm{Pb(Et)_3(c)} + \mathrm{C_2H_5(c)} \tag{1}$$

$$\mathrm{Pb(Et)_3(c)} \longrightarrow \mathrm{Pb(c)} + \mathrm{3C_2H_5(c)} \tag{2}$$

$$\mathrm{2C_2H_5(c)} \longrightarrow \mathrm{C_2H_4(g)} + \mathrm{C_2H_6(g)} \tag{3}$$

$$\mathrm{2C_2H_5(c)} \longrightarrow \mathrm{C_4H_{10}(g)} \tag{4}$$

$$\mathrm{C_2H_5(c)} + \mathrm{Pb(Et)_4(c)} \longrightarrow \mathrm{Pb(Et)_3(c)} + \mathrm{C_2H_4} + \mathrm{C_2H_6(g)} \tag{5}$$

The higher C_2–C_4 ratio ($3{\cdot}6:1$) observed with the shorter wavelength, 254 nm, is likely to be due to the greater probability of reaction (5) occurring. At this wavelength the photon energy is much in excess of that required for the dissociation of $PbEt_4$, resulting in the rate of reaction (5) increasing at the expense of reactions (3) and (4).

We acknowledge the support of this work by the Ministry of Technology.

(*Received, November 24th,* 1971; *Com.* 2023.)

---

[1] L. J. Rigby, *Trans. Faraday Soc.*, 1969, **65**, 2421.
[2] L. Riccoboni, *Gazzetta*, 1 H41, **71**, 696.