Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKII and V. A. SHISHKIN

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKII and V. A. SHISHKIN

STUDY OF THE ADSORPTION OF UNSATURATED FLUOROCARBONS C_2F_4 AND C_3F_6 IN AN ELECTRON PROJECTOR

Recently, a large number of works ($^{1-4}$) have been devoted to the origin of discrete bright spots appearing on the screen of an electron projector at gas pressures of $10^{-6} \div 10^{-5}$ mm Hg. For the present, only the direct connection of the spots with the adsorption of individual molecules may be considered established. On the basis of the dependence of the number of mobile spots on pressure, Müller (^{1}) believes that "molecular pictures" appear upon adsorption. By contrast, Becker (^{2}) relates their appearance to the transition of molecules directly bound to the substrate into a weakly adsorbed state. Both authors consider contact of the tip with gas at $p \gg 10^{-6}$ mm Hg to be a necessary condition. However, for vapors of solid substances this condition apparently is not obligatory, since Gomer (^{5}) observed "four-leaf clovers" of phthalocyanine at $p < 10^{-9}$ mm Hg and $\theta < 1$.

I. I. Tret' yakov (^{3}) adds, to the number of necessary conditions, exposure in the field in the presence of gas, which, in the author' s opinion, is necessary for the formation of microtips that increase the resolution. The results of comparing the form of spots arising upon adsorption of large organic molecules of different geometrical structure and different sizes (^{6}) indicate the absence of correspondence between the geometry of molecular pictures and the geometry of molecules. On the contrary, experiments with small molecules point to a definite correlation between the electronic structure of molecules and the shape of the spots (^{3}).

In particular, in work (^{6}) it was established that "pairs" and "rings" are observed only in the presence of a double bond, and four-leaf clovers with a more complex structure.

To explain this regularity, one of the authors (^{4}) advanced the hypothesis of the direct participation of the π-electrons of double bonds in emission with the formation of spots of complex shape, the principal role being attributed to bound biradicals formed during adsorption. The purpose of the present work was to test this hypothesis on chemically inert, stable molecules of unsaturated fluorocarbons, since for the unsaturated hydrocarbons studied previously there remained the possibility of radical formation through simple detachment of

Figure 1

Figure 1: Figure 1

hydrogen atoms upon contact with the tip and rupture of carbon bonds. In addition, it was desirable to specify a number of conditions necessary for the observation of molecular pictures.

Experimental Part

The studies were carried out on a conventional electron-projector setup. C_2F_4 and C_3F_6* were investigated. The method of admitting the gases was changed. The gas under study was first admitted at $p = 0.1$ mm Hg into an ampoule thoroughly degassed by heating in vacuum $\simeq 10^{-6}$ mm Hg.

activated charcoal. Before admitting gas into the projector, the ampoule offshoot was cooled with liquid air, after which the thin end of the ampoule was broken with the striker. By varying the temperature of the ampoule with the charcoal, it was possible reversibly to change the pressure in the system within the range 10^{-2}-$1 \cdot 10^{-7}$ mm. After the pressure had been reduced to $1 \cdot 10^{-9}$ mm and the initial pattern of clean W had been obtained, the experiment was begun. Figure 1 shows the stages of adsorption of C_3F_6 from a pressure of $1 \cdot 10^{-8}$ to $1 \cdot 10^{-6}$ mm. The first stages of adsorption resemble the adsorption of simple gases (O_2, N_2, H_2). The work function increases as the surface is filled. The first portions of gas make the image slightly granular; at a pressure of $5 \cdot 10^{-7}$ mm Hg, separate bright spots appear, fixed immovably in their places. At a pressure of $1 \cdot 10^{-6}$ mm, bright spots begin to appear, persisting for a limited time, at first only round ones and then "rings" and "halves." By the time mobile spots (molecular patterns) appear, the emission current falls by a factor of 13 (O_2 reduces it by a factor of 10^6 at $1 \cdot 10^{-7}$ mm). After this the emission current increases slightly. The total number of molecular patterns and the proportion of complex patterns increase with pressure (Fig. 3). A decrease in pressure always led to a reduction in their number. The entire pattern appears three-dimensional; the strongly emitting faces look multilayered and protrude above the dark ones. Holding in the field at a current of 20-25 μA ($p = 10^{-6}$ mm) leads to almost complete disappearance of the image contrast. If the tip is held at a pressure of $1 \cdot 10^{-5}$ mm and then the latter is reduced to $1 \cdot 10^{-7}$ mm, the number of spots gradually decreases. This shows that the molecular patterns are due to molecules weakly bound to

Fig. 1. Stages of adsorption of C_3F_6 on tungsten ($1 \cdot 10^{-8}$ mm $\div$ $6 \cdot 10^{-6}$ mm). $\tau = 1/10$ sec. a—clean tungsten tip at $p < 1 \cdot 10^{-9}$ mm, g—C_3F_6 at $p = 1 \cdot 10^{-6}$ mm; a, b, c—$U = 3.3$ kV; g—$U = 3.5$ kV.

* We take this opportunity to express our gratitude to Acad. I. L. Knunyants for providing these gases.

Fig. 4. Observed interconversions of molecular patterns of C_3F_6.

Figure 2: Fig. 4. Observed interconversions of molecular patterns of C_3F_6.

To the article by S. Z. Roginskii and V. A. Shishkin, p. 577

Fig. 2. Pairs of C_2F_4 on a reconstructed W tip. $U = 16.4$ kV, $\tau = 1/10$ sec.

Fig. 3. W tip in an atmosphere of C_3F_6 at
$p \simeq 5 \cdot 10^{-6}$ mm

To the article by I. A. Aleksina, p. 624

Fig. 1. Microphotograph of silt with a large number of diatom valves. Black dots are pyrite grains. Station No. 5308.

substrate. The filling of this layer depends on p. The heat of adsorption, estimated from the change in the lifetime of these patterns at 100° and 300°K, is ~ 700 cal/mole.

All the regularities described for the adsorption of C_3F_6 are also valid for the adsorption of C_2F_4, with the difference that the latter gas does not give circular rings. To clarify the necessity of using tips with small radii (because of the magnification) and the role of microtips in the detection of molecular patterns, the investigations were carried out both on sharp and on blunt tips ($0.1 \div 2.5\,\mu$). Even on an extremely blunt tip, which as a result of many hours of heating had acquired a rounded spherical shape, it was possible to observe barely distinguishable C_2F_4 doublets. For this, however, it was necessary to raise the pressure in the bulb almost to the point of discharge. Reconstruction of this tip in the field led to an increase (by ~ 5 times) in the size of the spots (Fig. 2). Adsorption on microtips formed during visualization by bombardment leads to the appearance of spots of almost the same shape as in adsorption on flat regions. The difference lies in the greater brightness of the spots on protrusions and in their lower sharpness. Sometimes distinct molecular patterns appear on the dark regions of the image.

Fig. 4. Observed interconversions of molecular patterns of C_3F_6.

It is probable that, at least for the given gases, filling of the surface plays a greater role than the possible formation of submicrotips. Microtips that lead to a noticeable local increase in emission do not play a significant role in this process. Admission of O_2 at $p = 1 \cdot 10^{-7}$ mm onto a tip covered with C_2F_4 led to a gradual decrease in emission and to a change in the distribution of light and dark regions to the characteristic oxygen pattern. Doublets were observed only in regions surrounding the (100) direction. This indicates the displacement of C_2F_4 by oxygen from layers directly bound to tungsten. In this case the form and behavior of the molecular patterns remain unchanged.

The lifetime of molecular patterns in the case of both unsaturated fluorocarbons studied is on the order of fractions of a second (rarely seconds). When the tip is heated, the flicker frequency increases until, finally, upon dark-red heating, the adsorption layer begins to run off rapidly in the form of very bright and large spots of blurred shape. Desorption into high vacuum does not lead to the formation of a carbon film; however, high-temperature heating ($\sim 2000°C$) in an atmosphere of C_3H_6 at $p = 1 \cdot 10^{-6}$ mm leads to appreciable deposition of a carbon film. When the mount with the tip is cooled with liquid nitrogen, the emission pattern becomes calm, and the lifetime of the spots increases to several seconds. It is possible to distinguish interconversion of forms (Fig. 4). Round spots, when transformed into doublets, increase in size; they undergo an even greater increase when changing into rings. Increasing the anode voltage reduces their lifetime.

Discussion of Results

1. The connection between the appearance of doublets and rings and the presence of a double bond has been confirmed on a new type of compound, and the possibility of repeated repetition without introducing new portions of gas has been shown.

2. The obligatory participation of microtips in the formation of molecular patterns has not been confirmed.

3. Rings were detected only for the less symmetric molecules C_3F_6.

4. The sharpness of the molecular images and their lifetime increase with decreasing temperature, owing to which it is possible to clearly observe transitions of the molecular images from one form to another.

5. The data obtained do not contradict the previously expressed hypothesis concerning the role of radicalization of π bonds. In this case, the formation of such radicals is allowed both upon adsorption in the volume directly adjacent to the tip and as a result of rupture of the π bonds of previously adsorbed molecules, with their possible transition, according to Becker, from the lower to the upper layer.

6. Explanation of the form of the observed images and of the mutual transformations of the forms on the basis of the simple geometrical considerations used by a number of authors is difficult ([1,2]). The fact that molecules that differ greatly in their structure reproducibly give images of one and the same form indicates that there is a deeper connection between the form of the spots and the electronic structure of the molecules. In particular, one might suppose that the molecular spots convey the probability of distribution of the electron clouds of those orbitals that participate in the formation of the π bond; the weak chemisorption character of the bonding of these molecules indicates that the broken bonds are not saturated by the surface, but are localized at the molecules themselves. Such a variant of the hypothesis is readily compatible with the previously proposed hypothesis concerning the role of π-electron bonds and with the experimental

data.

The authors express their gratitude to I. A. Bespalova for assistance in the work.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
9 VII 1959

CITED LITERATURE

[1] E. W. Müller, *Ergebn. exakt. Naturwiss.*, **27**, 290 (1953).
[2] J. Becker, Adsorption on Metal Surfaces, Collected volume *Catalysis, Electronic Phenomena*, IL, 1958.
[3] I. I. Tretyakov, Collected volume *Conference on Catalysis*, Moscow, 1958.
[4] S. Z. Roginskii, *ZhFKh*, No. 9 (1959).
[5] R. Gomer, D. A. Speer, *J. Chem. Phys.*, **21**, 73 (1953).
[6] I. I. Tretyakov, S. Z. Roginskii, *DAN*, **107**, 857 (1956).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.