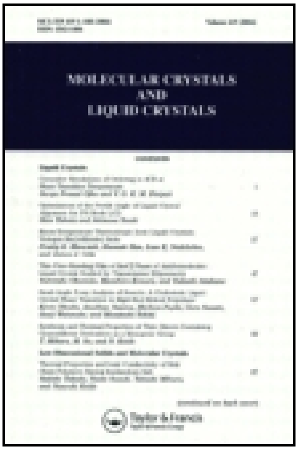

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GAS-SOLID REACTIONS IN BILAYER STRUCTURED SYSTEMS: EFFECT OF THE REACTION ON MONOLAYER PROPERTIES

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ABSTRACT: It was previously shown that gases can diffuse into amphiphilic substances that have a "stacked bilayer" type of crystalline structure. Several of the gases will react with any free radicals that may be present and the reaction can be monitored by ESR spectroscopy, (1-5). Nitrogen dioxide and similar gases will react with molecules possessing a double bond even in the absence of free radicals. In this communication it is shown that these reactions will affect, in specific ways, the monolayers formed from these substances.

INTRODUCTION

As was shown in previous communications (1-5), many gases are capable of diffusing into crystalline amphiphilic substances having a "bilayer" type of structure. If free radicals are present, for example those generated by radiation, gases such as oxygen, nitric oxide, nitrogen dioxide, or sulfur dioxide, will react with them. The reaction, and therefore the diffusion of the gas within the solid, can then be monitored by ESR spectroscopy. The substances used in previous experiments, (1), have the ability to form monolayers on the surface of water. It was thought that any effect these gas-solid reactions might have on monolayer properties could shed some additional light on the nature and extent of these reactions. As will be shown, principally by studies on stearamide and oleamide, the effects can be considerable, depending on the chemical nature of the amphiphile and the packing of the molecules in the solid and in the monolayer. These effects can serve as a sensitive indicator of the reaction. Some tentative conclusions will be drawn.

EXPERIMENTAL

For these experiments we used the same materials, recrystallized in the same fashion, as in the prior communication (1). In one group of experiments, stearamide and oleamide were put under vacuum in glass bulbs. Nitric oxide, oxygen or sulfur dioxide, under a pressure of 1/2 atmosphere, was then admitted and the bulb was sealed off. Except for the appropriate controls, the samples were irradiated at 15C in a ^{60}Co source at the rate of 450,000 rad per hour. A range of total doses was used. The samples were then stored overnight at 25C.

The monolayer experiments were done using a temperature controlled recording film balance designed and built at Brookhaven National Laboratory. The tray and the barriers were teflon coated. The film balance was mounted inside a glove box resting on a vibration isolation table. Triply distilled water was used to fill the tray. For the measurements, .02 gm. of material was dissolved in chloroform: hexane (1:1). The sample was introduced to the film balance by micro syringe and the solvent was allowed to evaporate for a period of at least 10 minutes before initiating any measurements. The pressure-area curves were run 24.5 C and at a sweep speed of 14 cm. squared/min. (1.2 Angstrom squared per molecule per minute). Unirradiated controls, kept under the appropriate gas for an equal period of time were also run.

In addition, we ran some preliminary experiments in which unirradiated stearamide, oleamide, elaidic acid and vegetable lecithin were cast as monolayers on the water surface. A 250 cc bulb was filled with nitric oxide at atmospheric pressure and the gas from it was then released over the surface. The change in area of the monolayer was then determined. For this experiment, the glove box was first flushed several times with nitrogen in an attempt to remove the presence of oxygen.

Finally, fresh monolayers of the same substances were made and a Tesla coil was held for 2 minutes, in air 20 cm. above the surface, to generate ozone. The change in area was again determined. Each of the above experiments was run in triplicate and in random order.

RESULTS AND DISCUSSION

Initially the results obtained with irradiated crystalline stearamide and oleamide will be described. These compounds were chosen because they represent opposite extremes of the types of behavior in which we were interested. The diffusion of gas into oleamide is very rapid. In stearamide it is slow (1). Unirradiated stearamide gives a condensed, "crystalline" type of pressure-area curve on the film balance whereas oleamide of 1/2 atmosphere, was then admitted and the bulb was sealed off. Except for the appropriate controls, the samples were irradiated at 15C in a ^{60}Co source at the rate of 450,000 rad per hour. A range of total doses was used. The samples were then stored overnight at 25C.

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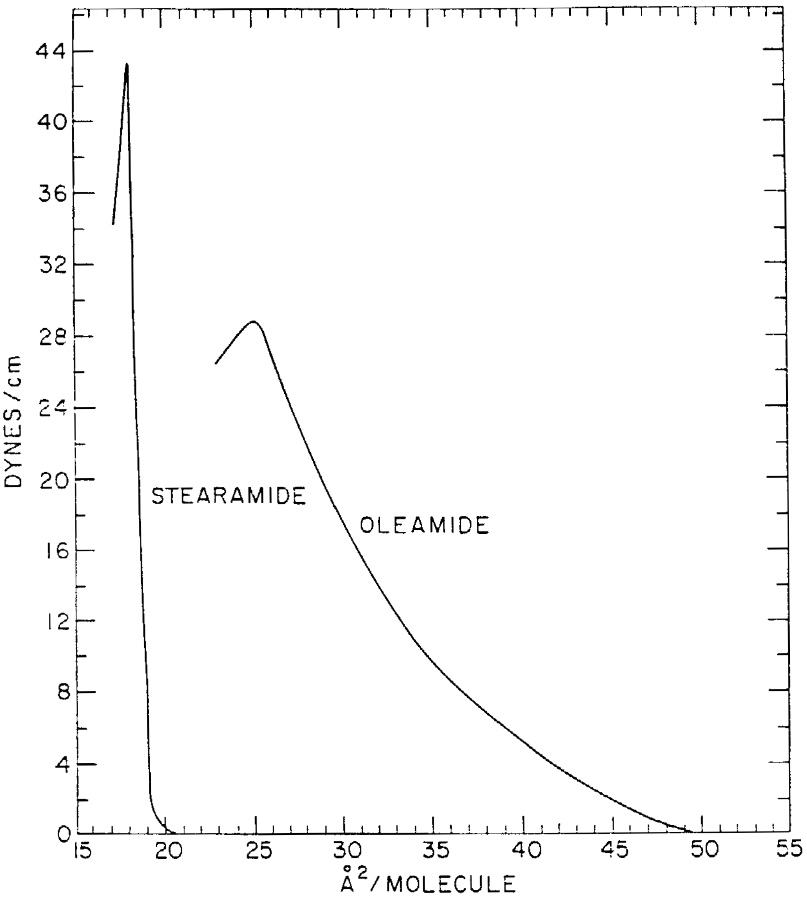
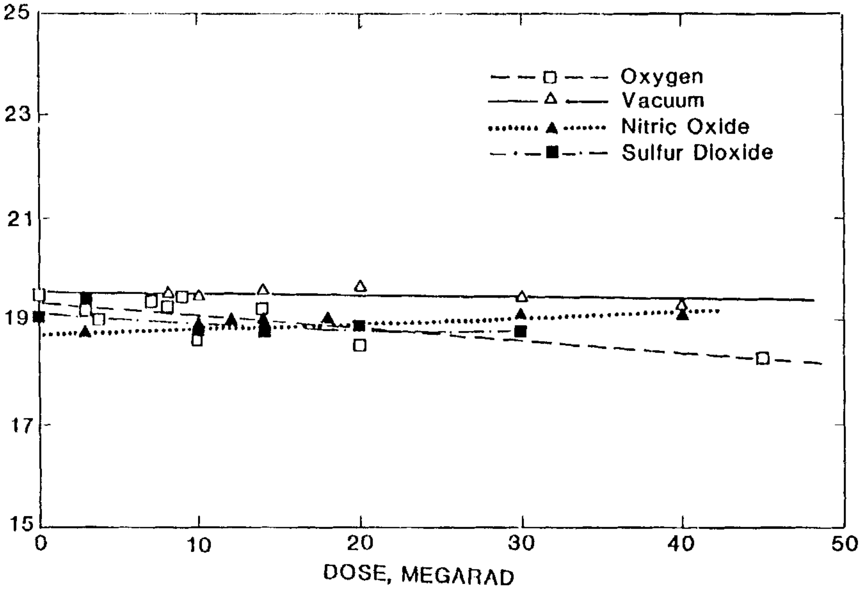


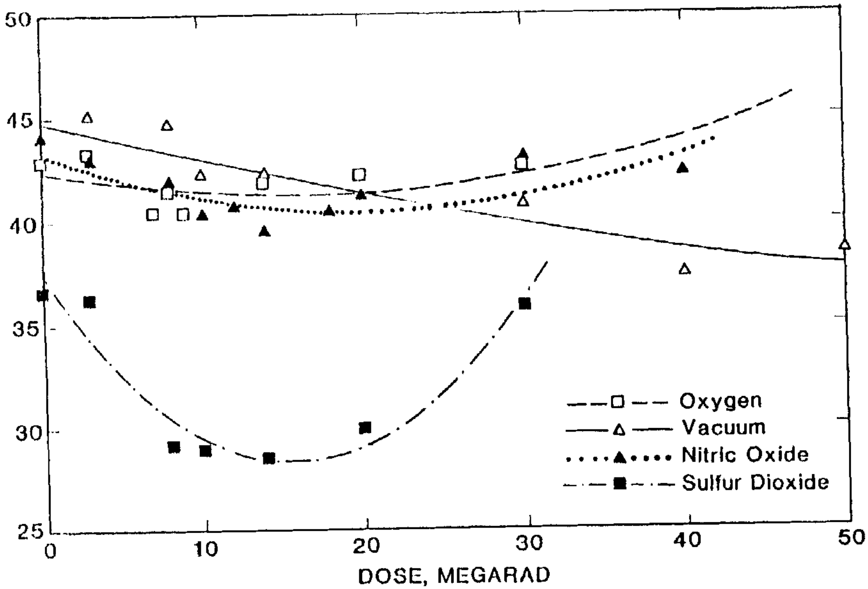
1. Pressure-area isotherms for untreated stearamide and oleamide monolayers.

yields an expanded "liquid" type of curve (Figure 1). This is probably because the saturated hydrocarbon chains of stearamide allows the molecules to pack efficiently whereas the cis double bond of oleamide produces a kink in the molecular chain which interferes with efficient packing, (1). After irradiation and reaction with gas, stearamide still showed a condensed type of pressure-area curve with only minor changes in the area per molecule (Figure 2). This was expected because of the slow diffusion in this compound and because the concentration of free radicals, even at the highest radiation dose used, was still relatively small. Oxygen showed the largest effect, probably because it initiated a chain reaction. Such chain oxidations were previously noted in related compounds (4).

Some interesting effects were observed when the monolayer pressure at the break point was determined (Figure 3). Except for the vacuum case, the data showed an initial drop in break pressure followed by a rise. The cause of this obviously lies with the molecules of the reaction product. A tentative explanation might be that the gas reacts with the free radical yielding a product molecule with a bulkier group at the reaction site than the hydrogen atom originally present. The product molecules then behave as defects in the "crystalline" two dimensional film of stearamide. Plausibly these initially decrease the yield strength of the monolayer in a manner similar to the effect of grain boundaries, dislocations and other defects in three dimensional systems. Perhaps, then, the subsequent increase in break pressure is due to a process similar to work hardening in metals in which the number of product molecules, behaving as defects capable of pinning dislocations in the monolayer, have increased to the point where they interfere appreciably with the glide of the dislocations. Of the gases used, sulfur dioxide is likely produce the largest effect since it adds the bulkiest side group. The effect of vacuum irradiation would appear to be different because, in the absence of gas, the free radicals would react by dismutation or recombination. This is a slow reaction as evidenced by the slow rate of decay of the free radicals under vacuum. In the solid dismutation would probably yield a trans double bond. Recombination would result in a cross link between two molecules. Neither of these reactions yields a bulky side group and neither of these is likely to interfere drastically with molecular packing. Perhaps, if the irradiation were carried to higher doses, an upturn in



2. Changes in area of stearamide in square Angstrom per molecule after irradiation in the presence of gas.

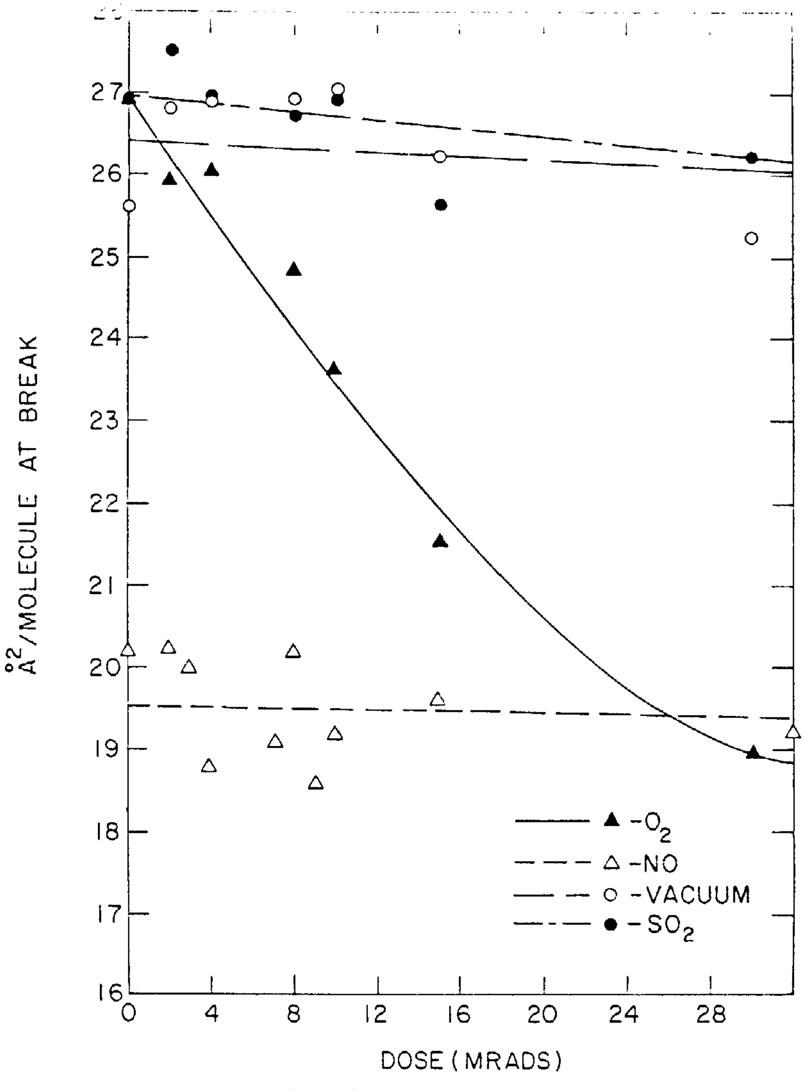


3. Break pressures of monolayers of stearamide exposed to gas and irradiated.

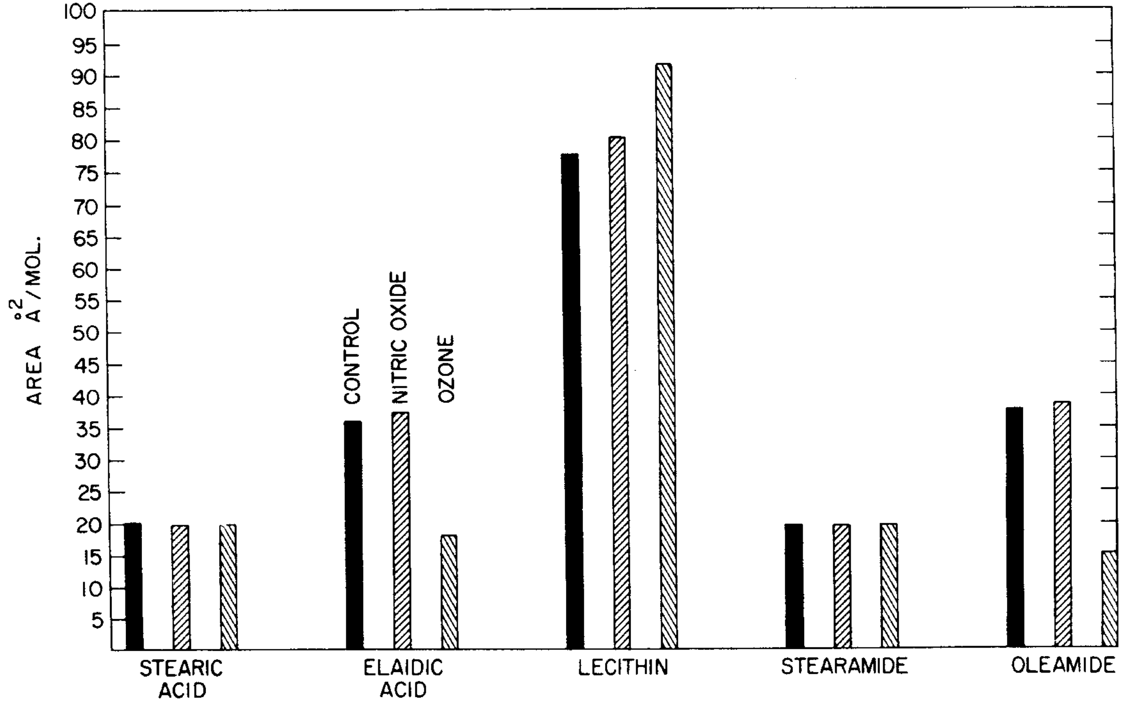
the break pressure would have been noted in the vacuum case also.

The behavior of oleamide presents a different picture. After exposure to radiation and gas, the form of the pressure-area curve also remained unchanged. The break pressure, initially considerably less than that of stearamide, (Figure 1), showed no change within the experimental error. This probably reflects the expanded nature of the monolayer which, therefore, can accommodate itself more easily to the presence of a small number of molecules with bulkier side groups than the more rigid "crystalline" stearamide monolayer. The yield strength of the monolayer thus would not be affected to any great extent.

When measurements related to the area per molecule were made, some significant effects were noted. Like stearamide, oleamide showed little change in area per molecule under vacuum irradiation or in the presence of sulfur dioxide. In the presence of oxygen, however, there was a steep decline in area with radiation dose, (Figure 4). With nitric oxide, on the other hand, the area decreased radically even in the absence of radiation. Irradiation produced no further changes larger than the experimental scatter, which in this case was somewhat larger than the other data, (Figure 4). The explanation of these effects may lie in the ability of these gases to diffuse rapidly into oleamide, (1). Oxygen is likely to initiate a chain oxidation reaction (4). The effect therefore would be multiplied many fold as compared to the sulfur dioxide reaction, for example. Most likely hydroperoxide and carbonyl groups are produced at the reaction sites (4). The molecules now have an additional polar group located in the middle of the hydrocarbon chain. In addition peroxidative cleavage of the molecule may occur, as has been postulated for cell membrane lipids in the presence free radicals and high partial pressures of oxygen, (6). This cleavage, by splitting the molecule into two smaller fragments, one with two polar groups and the other with one, would most likely bring about a small increase in the solubility of the compounds or, perhaps, in its ability to form micelles. In either case there would be a loss of material from the monolayer which would masquerade as a decrease in area per molecule. Another possibility is that the chain oxidation occurs at the double bond yielding an oxygen bearing group and a single bond at the site. The elimination of the cis double bond, and the kink in the aliphatic chain this bond causes,



4. Area per molecule of monolayers of oleamide exposed to gas and irradiated.



5. Relative change in area of monolayers exposed to gas.

might allow the molecules to become relatively straighter and occupy less space on the surface despite the bulkier side group.

As noted above, oleamide shows a dramatic decrease in apparent area per molecule in the presence of nitric oxide which is independent of the presence of free radicals or radiation. This supports the hypothesis, previously suggested on the basis of ESR data (1), that nitric oxide will react with the compounds possessing double bonds even in the absence of free radicals. If the nitric oxide reacted directly, each reacted molecule would have two strongly polar groups. Another possibility is that the nitric oxide, upon adding at the double bond or perhaps catalyzing a cis-trans isomerization, unkinks the aliphatic chain allowing it to straighten. It is known that nitrogen dioxide can cause cis-trans isomerization in olefins (7, 8). It has been suggested that nitric oxide will not react in the absence of nitrogen dioxide. Although we used research grade nitric oxide, we cannot rule out the presence of trace amounts of nitrogen dioxide.

Finally, we describe the group of experiments in which monolayers of the appropriate compounds were exposed to various agents without prior irradiation. Despite repeated flushing of the dry-box with nitrogen prior to the experiment, we noticed the formation of brownish vapor when the nitric oxide was admitted, thus indicating that some oxygen was still present and that nitrogen dioxide formed. As expected, stearic acid and stearamide showed negligible change in the pressure-area curve or the area per molecule, (Figure 5). Oleamide, elaidic acid and lecithin have double bonds. The lecithin and elaidic acid, like oleamide, yielded expanded pressure-area isotherms on the film balance. Surprisingly, these three compounds showed a small but significant increase in area per molecule upon exposure to nitric oxide. The reason for the difference between these results and the ones obtained above are obscure because of the limited amount of data presently available. Perhaps the nature of the reaction products was changed lue to the presence of water and the large amounts of nitrogen dioxide which resulted from the reaction of the nitric oxide with the residual oxygen present in the glove box. It is known that oxygen will enhance the reaction with the nitrogen dioxide with hydrocarbons. Possibly, also, the addition of a nitroxy group at the middle of the molecule did not appreciably increase solubility but instead allowed the molecule to bend over so that the new polar group faced the water surface. Thus there would be an apparent increase in area per molecule. If such a process were in competition with the cis-trans isomerization mentioned above, the increase in area would be rather small.

The electric discharge of the Tesla coil above the monolayer generated ozone. As is seen in Figure 5, there was negligible effect of the gas on stearamide and stearic acid which have no double bonds. The three compounds with double bonds, on the other hand, showed marked changes indicating that they reacted with the ozone. Oleamide and elaidic acid showed dramatic decreases in area per molecule whereas lecithin gave a large increase.

Ozone cleaves double bonds, (9), splitting the molecule into two smaller ones each with a polar group at the newly formed end. As suggested above for peroxide cleavage, the smaller product molecules produced from elaidic acid and oleamide probably show increased solubility in water and therefore loss of material from the monolayer.

The case of lecithin is somewhat different. A possible reason for the increase of area with ozone lies in the fact that natural lecithin in general has two hydrocarbon chains only one of which is unsaturated. The ozone cuts the unsaturated chain at the double bond leaving a polar group such as carboxyl or carbonyl on the end of the shortened hydrocarbon chain which remains attached to the lecithin molecule. The molecule is still as insoluble due to large unreacted hydrocarbon chain which remains on the molecule. If the remanent chain can bend over so that its new polar end group faces the water, the result would be an apparent increase in area per molecule. Such an explanation would be consistent with the decrease in area shown by the other two compounds.

It is interesting to note that the change in area of oleamide and elaidic acid in the presence of the nitrogen oxides and the ozone are approximately equal. This suggest that the cis and trans double bonds are equally reactive and that the differences in reaction rate of the crystalline material with gas noted previously, (1), is solely due to differences of diffusion rate in these solids.

Something should be said about the reproducibility of these experiments. Keep in mind that this was an exploratory investigation. Each experiment was done in triplicate and in random order. The data was handled by least squares techniques. With the same batch of compound the reproducibility was good. However, from batch to batch, the reproducibility was poorer quantitatively but, qualitatively, the results were unequivocal. Quantitatively there is evidence that the results show some dependence on trace impurities, lattice defects, etc. For example, despite recrystallization, batches of material obtained from different sources gave somewhat different quantitative, though identical qualitative, results. Material shock cooled from the melt showed slightly larger diffusion rates than material grown slowly. However, qualitatively, the trends were unmistakable. The results for oleamide, for example, could never be mistaken for those from elaidic acid or stearic acid or stearamide. This is backed up by many more experiments with more compounds than are discussed here.

CONCLUSIONS

The type of material with which we were concerned is exemplified by amphiphilic substances such as fatty acids, fatty amides, phosolipids, many surfactants and similar materials. We showed in a prior communication, (1), that gases can diffuse into crystalline solids having a particular type of "stacked bilayer" structure. It was demonstrated that gases such as oxygen, nitric oxide, nitrogen dioxide and sulfur dioxide will diffuse into these solids and will react with any free radicals that may be present, such as those resulting from radiation damage. Previous work with smaller amides, (4), suggest that oxygen in such circumstances, may initiate a chain reaction with a kinetic chain length that can reach over 100. If double bonds are present, the oxides of nitrogen will react with the material even in the absence of free radicals. There was also evidence that the presence of oxygen will enhance this reaction. The work described in this communication shows that these gas-solid reactions can radically alter the physical characteristics of monolayers made from these materials. These changes are consistent with the ideas expressed in reference (1) and could possibly serve as an indicator of the nature of the reaction that had taken place. In addition, it was also demonstrated that gases such as ozone and the oxides of nitrogen will directly affect previously formed monolayers even in the absence of free radicals, causing significant changes.

Though the gases used in these experiments were not chosen with that in mind, it turns out that, except for oxygen, they were all ones that are of concern in air pollution. The type of substance we used has great industrial and biological importance. Lecithins, for example, are important constituents of cell membranes. As noted in reference (1), preliminary chemical analysis indicated the presence of peroxides in material exposed to the oxides of nitrogen. Others have made similar findings, (10, 11). It has been reported that peroxides were found in the membranes of animals exposed to nitric oxide, (12). It has been postulated that peroxides generated during such exposure alter the "fluidity" of membranes, (6). This suggests that the studies such as the ones described in this and the previous communication, besides shedding some light on solid state reaction mechanisms, may in addition be useful, easily obtained, bulk models for studying some problems involving cell membrane lipids. This is supported by some crude preliminary experiments we did using lung surfactant washed from the lungs of rats and calves. The gas-solid reactions might also provide a means for the synthesis for some interesting new surfactants.

It should finally be emphasized that the work described here and in the previous communication is of a preliminary nature and that the proposed mechanisms and explanations must be considered tentative in nature. They are presented here solely for the purpose of suggesting to others the potential usefulness of this kind of study.

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