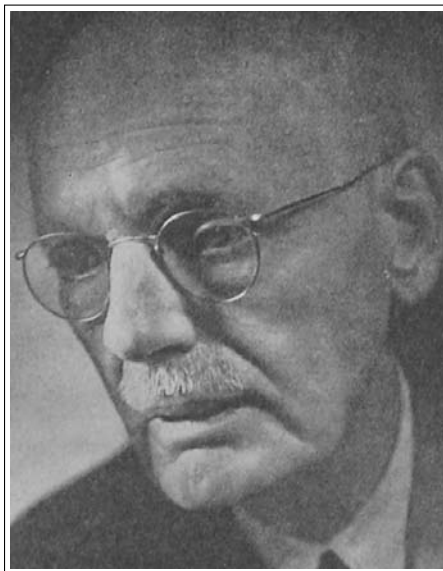


## THE HISTORY OF OZONE. VI. OZONE ON SILICA GEL (“DRY OZONE”) (1)

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### Introduction

As part of a general study of the interaction between gases and solids in the laboratory of Alfred Magnus (Fig. 1) at the University of Frankfurt, Magnus and Grähling (2) reported the adsorption of ozone on silica gel in 1929. These measurements were complicated by the thermal instability of ozone, which, as shown by Magnus and Grähling, was further catalyzed by silica gel. A second problem was the low concentration of ozone in oxygen obtained from conventional ozone generators. Nonetheless, Magnus and Grähling found that considerable amounts of ozone could be adsorbed on silica gel at low temperatures where decomposition was not a problem. The average heat of adsorption of ozone, measured by taking the difference between pure oxygen and ozone-oxygen mixtures was 5,600 cal/mole with a temperature coefficient of -175 cal/deg. The corresponding values for oxygen were 3,200 cal/mole and -30 cal/deg. Thirty years later Cook et al (3) performed a similar study with results in agreement with those of the earlier work. They measured the adsorption isotherms (Fig. 2) for ozone on silica gel over the range -78.5° C to -140° C as a function of ozone

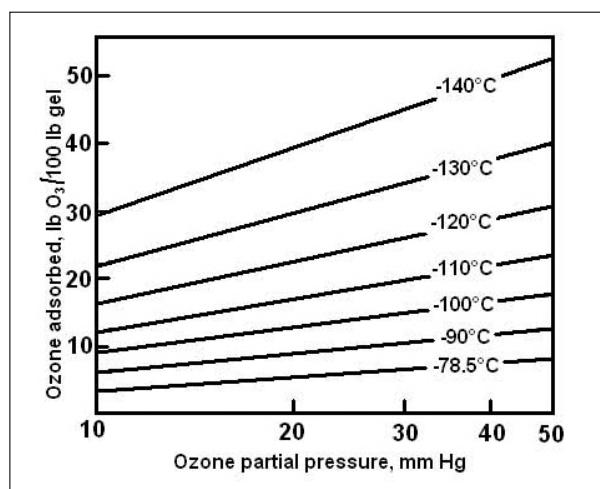


*Figure 1. Alfred Magnus, Un. of Frankfurt, 1880-1960.*

partial pressure. As can be seen in Figure 2, adsorption increased markedly with decreasing temperature, the significance of temperatures below the boiling point of ozone (-112° C) is not clear. The measurements were made by passing ozone-enriched oxygen (ca 2% ozone) from a silent discharge apparatus through a tube packed with silica gel until compositions of the entrance and exit gases were identical. The ozone was then desorbed and analyzed iodimetrically.

More recently Atyaksheva and co-workers (4) have studied the adsorption of ozone on silica gel in considerable detail. Bulanin et al. (5) reported that the IR spectrum of different isotopic ozone species on silica gel at 80 K exhibited hydrogen bonding of terminal oxygen atoms with silanol groups but that only minor changes from the spectrum of pure liquid ozone were observed. The only report on the long-term stability of ozone on silica gel is due to Hesse and Bayer (6) who claimed that 91% of adsorbed ozone was retained after 2 weeks storage at -75° C (but see below).

Silica gel is well-known to have a high affinity for water; commercially supplied silica gels used in most of the work described here generally contained about 3% water. This can be reduced by heating under vacuum.



**Figure 2.** Adsorption isotherms for ozone on Davison silica gel at  $-78.5^{\circ}\text{C}$  to  $-140^{\circ}\text{C}$  and total pressure of 1 atm. Reprinted with permission from Ref. 3. Copyright 1959 American Chemical Society.

Cook et al reported that the adsorption capacity of silica gel which was repeatedly recycled with ozone enriched oxygen was reduced markedly but could be regenerated by heating in vacuo; they attributed this to accumulation of water on the silica gel. Ishii et al (7) claimed that concentrations of 1-2% water on silica gel decreased the rate of decomposition at  $-80^{\circ}\text{C}$  significantly. The function of adsorbed water as a reagent for ozonide decomposition will be mentioned in the section on organic reactions.

### Desorption

A number of simple procedures are available for desorbing ozone from silica gel. These include passing a gas (not necessarily oxygen) through the silica gel, warming above the temperature at which adsorption occurred (microwave heating has also been used (8)), reduction in pressure, or a combination of these. Thus there is considerable flexibility in the desorption process. While Hesse and Bayer (6) reported in 1964 that 95% of the adsorbed ozone could be recovered by desorbing with a stream of nitrogen gas, it is not clear if the 5% loss is characteristic of desorption or was due to losses in the manipulations required for analysis. We note that a similar loss was observed by Riesenfeld and Schwab (9) in analyses of highly purified ozone. Edgar and Paneth (10) made a careful study and concluded that there was complete recovery of ozone adsorbed at liquid oxygen temperature; desorption was effected by warming to  $-120^{\circ}\text{C}$  in a stream of oxygen. Other workers seem to have assumed, without experimental verification, that desorption is quantitative.

Although desorbed ozone seems to be perfectly normal in its chemistry, it has variously been reported to contain singlet oxygen (11) or to consist of clusters of ozone (12, 13). The latter workers also reported theoretical calculations in support of the existence of  $\text{O}_6$  and  $\text{O}_9$ . These reports have not elicited any response.

### Storage of Ozone

Examination of Fig. 1 shows that even the few percent of ozone in oxygen provided by conventional ozone generators, when adsorbed at the convenient temperature of approximately  $-78^{\circ}\text{C}$  (14), will achieve a loading of 5-10% by weight of ozone on silica gel; this ozone is quite stable if maintained at low temperature. Bailey and Reader (15) estimated that the ratio of ozone to oxygen is on the order of 8,000:1 while Cook et al (3) stated that "very little" oxygen was adsorbed. Furthermore, convenient procedures are available for desorbing the ozone when desired. These facts combined to provide an attractive possibility for storing ozone on silica gel for use when desired, provided that this can be done safely. The Linde company, worldwide purveyors of gases, made a significant investment in this possibility.

The first report in the direction of safe storage was due to Cook et al (16) at Linde in 1956 who tested the explosion hazard of silica gels containing adsorbed ozone by igniting an electric spark within or above the solid material; they reported that loadings of up to 10% of ozone did not present an explosion hazard. They went on (3) in 1959 to describe a pilot plant for storage of ozone. This consisted of three 6" diameter aluminum tubes each filled with 125 lbs of Davison silica gel to a height of 15 feet. Cooled ozone in oxygen, as produced by a Welsbach generator (2% ozone), was passed through the cooled columns until saturation. Oxygen was recycled in the closed system and the ozone was desorbed by evacuation. An alternative method for desorbing ozone, warming, was not practical with large columns. After 200 hours operation, the capacity of the silica gel was reduced by 50%, presumably because of adsorption of water vapor as noted above. The authors concluded that the method described provides a reasonable procedure for storing ozone for use on demand. A 1975 Japanese patent (17) makes pikers out of Cook et al. It describes a system operating at  $-80^{\circ}\text{C}$  containing tons of silica gel with the corresponding 10% of ozone. Desorption was effected by nitrogen gas and the operational parameters were adjusted so that the ozone concentration in the effluent gas mixture remained nearly constant.

One application of such storage is for so called "load leveling" (18, 19). The ozone production unit in, for example, a water purification plant, need not be designed to meet peak demand but only to produce the average amount of ozone required. When demand is low, the excess production can be stored to be available when required.

Cook et al (3) also suggested that it might be possible to provide adsorbed ozone in cylinders in the same manner used for supply of other gases. However, as they pointed out, it would be necessary to keep such cylinders at low temperature and provide special safety features in the event of failure of the cooling system. To the best of our knowledge, this has not proved to be a practical procedure although a Japanese patent (20), without safety features, exists.

A method for water purification described by Tizaoui and Slater (21) involved contacting a bed of ozone adsorbed on silica gel with the water to be purified; the silica gel was regenerated by heating after use. An ingenious application for liquid purification was described by Leitzke (22) in which desorption of ozone from silica gel was achieved by the vacuum from an injection pump using the liquid to be purified (drinking water, waste water e.g.) so that the desorbed ozone was introduced directly into the liquid.

In addition to the use for water purification mentioned above, a number of other applications of ozone on silica gel have been described. These include (1) analysis of atmospheric ozone, (2) changing the composition of the ozone stream, and (3) use in organic chemistry.

### (1) Analysis of Atmospheric Ozone

Concentrations of ozone found in the atmosphere often lie at or below the limit of sensitivity of the conventional iodimetric determination; this method also suffers from a lack of specificity for ozone. These problems were overcome using adsorption of ozone on silica gel by Paneth and Edgar (23) and by Briner (24) independently in 1938, nine years after Magnus and Grähling's original report. Paneth and Edgar accumulated the ozone from 1,000-1,500 liters of air by adsorption on specially prepared silica gel at liquid oxygen temperature ( $-183^{\circ}\text{C}$ ), thus multiplying the amount of ozone manyfold. Desorption was achieved by warming to  $-120^{\circ}\text{C}$  in a stream of oxygen. Control experiments showed (10) that complete recovery of ozone was achieved under these conditions. The desorbed gas was shown to be ozone by

use of tetrabase paper and by spectroscopy, and subjected to iodimetric analysis. Adsorbed nitrogen dioxide was not affected but could be desorbed at higher temperature (they used boiling water) and analyzed. After a very detailed preliminary study (10) Edgar and Paneth (25) found that the ozone concentration in London air was in the range 0.4-4.5 ppm and the nitrogen dioxide concentration in the range 0.05-2.0 ppm. This procedure for ozone analysis was also used by Jacobi (26) who passed 2000 l of air over silica gel at liquid oxygen temperature and by Sadikov (27) who found a value of  $0.8 \times 10^{-8}$  g/l for the ozone concentration in his sample of air.

In the early days of smog studies in Los Angeles, Littman and Marynowski (28) were able to show that ozone is the principal oxidant in the Los Angeles atmosphere; they flushed the adsorbed gases from a large sample of air into an optical cell and identified ozone spectroscopically.

### (2) Changing Composition of the Ozone Stream

When ozone generated from pure oxygen is adsorbed on silica gel, ozone of high purity is retained on the silica gel. This is probably the simplest way to obtain pure ozone since the low temperature condensation procedure commonly used invariably gives an ozone-oxygen mixture which requires further manipulation to obtain oxygen-free ozone. The first application of this fact was due to Bailey and co-workers (15, 29) in 1961 who required oxygen-free ozone in order to establish if oxygen was formed in the course of an ozonolysis reaction. They performed the desorption using nitrogen gas to obtain a stream of ozone in nitrogen; a conventional oxygen analyzer was then used to determine if oxygen had been formed in the ozonolysis. Hesse and Bayer reported (6) that they used such a procedure routinely in ozonolysis of organic compounds; problems arising from the presence of oxygen during the ozonolysis were avoided. Appropriate adjustments of temperature and gas flow allow good control over the composition of the ozone stream giving considerable flexibility in experimental procedures.

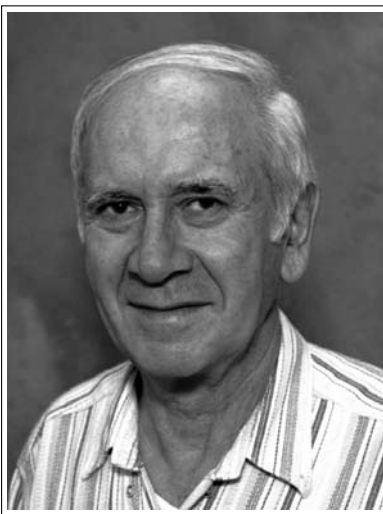
It is also possible, using warming or reduced pressure, to desorb ozone and obtain a stream of pure ozone of desired pressure. This procedure has been used by, among others, Coleman et al (30) for growing films of  $\text{Ba}_2\text{YCu}_3\text{O}_7$  and by Sukuzaki et al (31) for treating stainless steel fiber.

### (3) Organic Chemistry (“Dry Ozone”)

The application of ozone on silica gel to organic compounds was developed by Yehuda Mazur (Fig. 3) and coworkers (32) at the Weizmann Institute of Science who published about 20 papers on the subject over a ten year period beginning in 1975. They coined the term Dry Ozone for these reactions to emphasize the fact that ozonolyses of organic compounds were performed on silica gel in the absence of any solvent. This procedure avoids possible complications from solvent and excess oxygen. Two additional factors involved are the reduced mobility of reaction intermediates and the possibility of conformational restrictions due to interactions with silica gel.

Shortly after the Mazur papers began to appear, a number of reports, mainly concerned with regioselectivity of hydroxylation reactions were published by A. L. J. Beckwith (Fig. 4) and co-workers (33) at the University of Adelaide and ingenious applications of Dry Ozone to compounds containing a cyclopropane ring and a variety of polycyclic compounds appeared from the laboratory of A. de Meijere (Fig. 5) et al at the University of Göttingen.

The simple general procedure used is illustrated by the 1986 Organic Syntheses (34) preparation of 1-adamantanol (**2**) from adamantane (**1**) in nearly 90% yield. This reaction is a general one; hydrotrioxides (ROOOH) have been shown to be intermediates (35, 36). The substrate is adsorbed on silica gel by rotary evaporation at reduced pressure of a mixture of silica gel and a solution of substrate in a volatile solvent, cooled in a Dry Ice-2-propanol bath (14), and ozone-enriched oxygen flowed through the vessel at this temperature until the deep blue color of ozone develops. Free warming to room temp. is followed by elution of product(s) with the appropriate solvent. Minor products in the reaction of **1** (<7%) were 2-adamantanone



*Figure 3. Yehuda Mazur, Weizmann Institute of Science, 1925-2004*

and adamantan-1,3-diol. We note that an important variable in these reactions seems to be the presence of water which normally constitutes a few percent of commercial silica gels; this may be reduced to a much lower value by heating in vacuo.

The reactions of organic compounds with Dry Ozone were reviewed briefly in 1979 by de Meijere (37) and extensively in 1983 by Mazur's co-workers, Keinan and Varkony (38). We will not attempt to repeat these reviews but rather present a few examples illustrating the novelty and utility of this relatively simple modification of the conventional ozonolysis procedure.

The selective oxidation at tertiary positions illustrated by the adamantane reaction was a general phenomenon and occurred with retention of configuration. The exceptions were substances having a methylene group adjacent to a cyclopropyl ring, as illustrated for the reaction of ethylcyclopropane (**3**) with Dry Ozone. The single product (95% yield) was methyl cyclopropyl ketone (**4**). De Meijere and Proksch, who reported this result (39), applied it to a variety of substances containing a 3-membered ring including the conversion (40) of hydrocarbon **5** to diketone **6**. This was subsequently transformed in 16% overall yield to the 6-rotane **7**. The de Meijere group investigated the reactions of a variety of polycyclic systems with Dry Ozone including studies of regio- and stereoselectivity and succeeded (41) in the first synthesis of a “hyperstable” bridgehead olefin.

The restricted mobility enforced by the adsorbent is nicely illustrated by the results of Den Besten and Kinstle (42) in the ozonolysis of pentene (**8**). In pentane solution this reaction affords a mixture (80% overall yield) of three ozonides representing all possible combinations of the intermediates, acetaldehyde and propionaldehyde with zwitterions **10** and **11**. In contrast, Den Besten and Kinstle, using Dry Ozonation with silica gel dried at 300° C under vacuum, obtained over 90% yield of the single ozonide **9**. Presumably the carbonyl and zwitterionic fragments produced



*Figure 4. Athelstan Lawrence Johnson Beckwith, Australian National University, b. 1930.*

were sufficiently restrained by the medium to combine before separating as they do in solution. In this and in alkene reactions in general with Dry Ozone the peroxidic products observed in solution reactions are generally not formed.

In many cases, final products of ozonide decomposition, aldehydes, ketones, and or carboxylic acids were observed in alkene reactions (42, 43) with ozone on silica gel. This is presumably effected by water present in the silica gel reacting with the ozonide. Decomposition with water was the earliest method used for obtaining the stable, final reaction products in many ozonolysis reactions.

Finally, Keinan and Mazur (44) studied the oxidation of amines to nitro compounds in considerable detail. This conversion was exploited by Giuliano and Diesenroth (45) in a key step of a synthesis of **13** where the amino group in **12** was converted to a nitro group in 80% yield.

In the nearly 25 years following the 1983 review (38) on Dry Ozone, only a few papers have appeared on the subject. Mazur became absorbed in the reactions of atomic oxygen with organic compounds, Beckwith became very much involved in free radical chemistry, and de Meijere turned to new cyclic systems and other aspects of his multi-faceted research program. The few papers which did appear included work on a synthesis in the sugar series (46), reaction of phenanthrene (47), of 2,3-di-*t*-butylbutadiene and monoterpenes (48, 49), of aromatic compounds (50), and the adamantane reaction (51-53). We have found no references to organic reactions involving ozone on silica gel after 1997. For the period 1980-2007, SciFinder affords a total of over 10,000 references to ozonolysis but only 52 to the combined terms ozonolysis silica gel. In view of the simplicity of the procedure and the clean reactions observed in many cases, it is puzzling to find that the application of Dry Ozone to organic compounds appears to have disappeared from the current chemical literature.

Replacement of silica gel by polyethylene (48, 49) favors isolation of ozonides, perhaps because of the minimal amount of water present. Ozone is also adsorbed on high silica zeolites (54). While fundamental studies have not been reported, a variety of applications have



*Figure 5. Armin de Meijere, University of Göttingen, b. 1939.*

been described, most of them appearing in the patent literature, including destruction of ozone, application to purification of water, and preparation of high concentration ozone

### Summary

Considerable amounts of ozone can be adsorbed on silica gel at low temperature. Loadings of up to 10% ozone do not represent an explosion hazard if maintained at these temperatures and are stable for extended periods of time. Desorption of ozone can be effected by flowing a gas through the silica gel, by raising the temperature, or by reducing the pressure. Applications of adsorbed ozone include storage of ozone, water treatment, analysis of very low concentrations of ozone found in the atmosphere, changing the composition of the ozone stream, and eliminating some of the complications observed in organic reactions. Adsorption of ozone on silica gel provides a simple means for obtaining high purity ozone. Adsorption of ozone on polyethylene and on high silica zeolites has also been reported.

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