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# THE DECOMPOSITION OF CARBON MONOXIDE IN CORONA DISCHARGE

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The decomposition of carbon monoxide in a corona discharge has been studied and the qualitative analysis of resulting products has been made by IR absorption spectrometry and mass spectrometry. From the results it follows that no gaseous reaction products are formed in sufficient concentration. The only reaction products are the mixture of dimers and polymers in form of a dark deposit on the inside electrode.

## РАЗЛОЖЕНИЕ ОДНООКИСИ УГЛЕРОДА В КОРОННОМ РАЗРЯДЕ

В работе приведены результаты изучения разложения одноокиси углерода в коронном разряде. Качественный анализ возникающих продуктов проведён при помощи масс-спектроскопии и инфракрасной спектроскопии. Из полученных данных следует, что в реакции не образуется в достаточной концентрации никаких газообразных продуктов. Единственным продуктом реакции является смесь димеров и полимеров в виде тёмного налёта на внутренней стороне электродов.

## I. INTRODUCTION

In this contribution we want to solve the problem of chemical reaction in a corona discharge. Carbon monoxide was chosen as a gaseous medium, because it is not only the essential constituent of the exhaustgas of cars, but also a not negligible part of the exhaustion of thermal power stations. When we take into consideration the hight toxicity of carbon monoxide (it bonds on hemoglobin 210 times faster than oxygen) we can see unfavourable prospects for living organisms in town and industry centres.

## II. EXPERIMENTS

The experimental apparatus used for the measurement of the decomposition of CO in a corona discharge consists of: 1) a discharge tube with a cylindrical configuration of electrodes (the inner wire of radius 0.1 mm; radius of the outside electrode 12.5 mm and length of wire 1 m); 2) an electrical circuit presented in Fig. 1; 3) a vacuum system illustrated in Fig. 2; 4) additional equipment (spectrophotometers UR-10 by Carl Zeiss and Perkin Elmer 180, quadrupole mass spectrometer QMS 101 by Balzers).

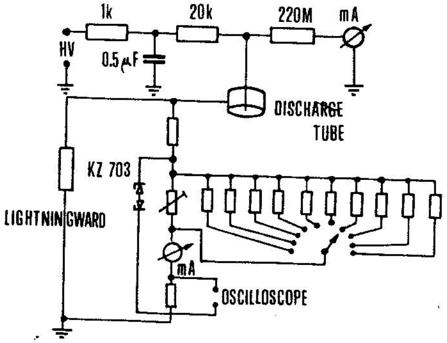

Fig. 1. Scheme of the electrical circuit (HV is the 80 kV high voltage source; a resistance 220 M with mA is used for measuring high potential; switch S with connected resistance and KZ 703 is used as an overload protection of the milliampermeter).

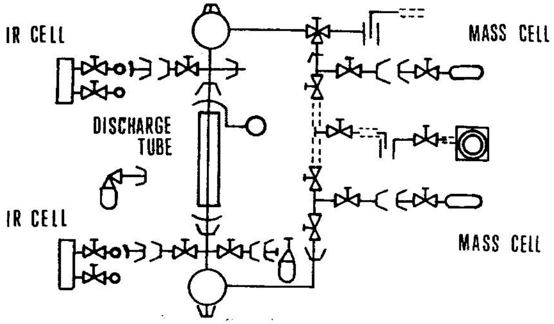

Fig. 2. Scheme of the vacuum system.

During the measurement we have sampled the gaseous product by using: 1) spectroscopic 10 cm cells with KBr windows for IR measurements; 2) glass cells for mass analysis. For the IR analysis of solid products we have used the KBr tablet making technology [1].

The first measurements were made in the positive corona discharge. We have scanned the $I$—$V$ characteristics of the discharge. The pressure of CO was maintained about 88 kPa. From the data obtained we have made the reduced I—V characteristics as shown in Figs. 3, 4. After a period of about 45 min. of running the corona discharge in CO with the parameters: voltage $V = 10$ kV and current $I = 1.7$ mA, we had to stop the discharge because of repeated breakdowns (sparks)

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in the discharge tube. This effect was caused by the formation of a deposit on the inside electrode. The gaseous reaction products and the deposit have been completely analysed. The methods used will be described later. Some measurements in a negative corona discharge were also made. The same apparatus as the previous one was used. We have scanned the *I*—*V* characteristics of the negative corona discharge first. A strange effect was observed. The current was increasing rapidly without the change or with a very small change of applied voltage. Three curves obtained illustrating this phenomenon are presented in Fig. 5. From previous behaviour we conclude that the negative corona discharge is changing into the high pressure glow discharge. After a period of about 30 min. when the corona discharge was running at a very small current of about 1—2 mA the discharge was changing to the high pressure glow discharge with an increase of the current up to 8 mA. Then the reaction products were studied. There was also observed a dark deposit as in the case of the positive corona discharge on the inside electrode. The gaseous reaction products and the deposit were analysed by the same methods as in the case of the positive corona discharge. The following methods were used:

1) IR absorption spectrometry for the samples of gaseous products from the cells placed beyond and below the discharge tube (the discharge tube has a vertical orientation). The spectra obtained can be seen in Figs. 6, 7 for the positive corona

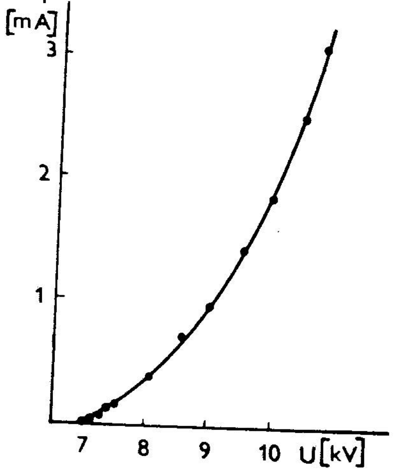


Fig. 3. *I* — *V* characteristics of the positive corona discharge in CO at the pressure 88 kPa.

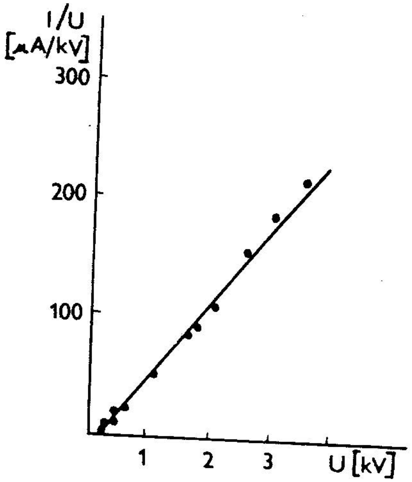


Fig. 4. Reduced *I* — *V* characteristics of the positive corona discharge in CO at the pressure 88 kPa.

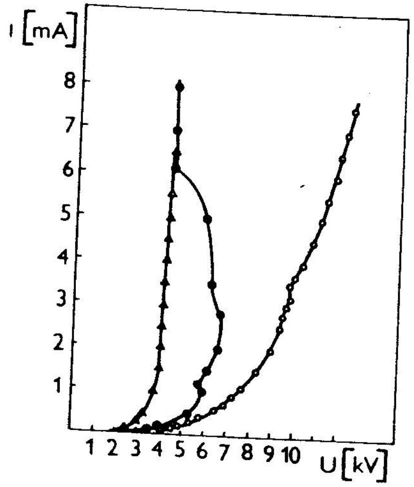


Fig. 5. *I* — *V* characteristics of the negative corona discharge in CO at the pressure 88 kPa; ○ at the beginning of the measurement, ● after 5 minutes, △ after 20 minutes.

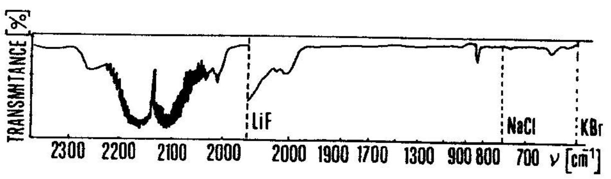


Fig. 6. IR absorption spectrum of the gaseous products from the cell placed beyond the positive corona discharge tube.

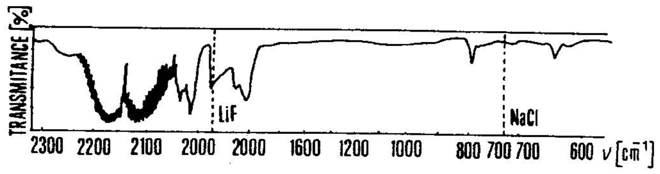


Fig. 7. IR absorption spectrum of the gaseous products from the cell placed below the positive corona discharge tube.

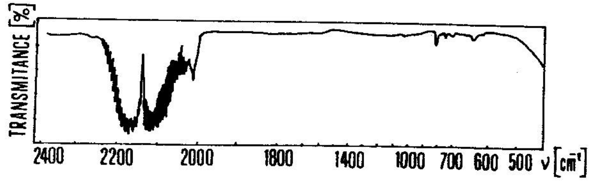


Fig. 8. IR absorption spectrum of the gaseous products from the cell in the case of the negative corona discharge.

discharge and in Fig. 8 for the negative corona discharge. The reference IR absorption spectrum of CO from the pressure tank is in Fig. 9.

2) Mass spectrometry for the gaseous products.

3) IR absorption spectrometry for the solid deposit on the wire was also used.

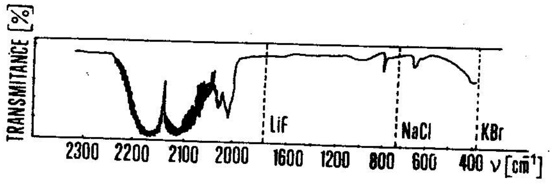


Fig. 9. The reference IR absorption spectrum of the CO from the pressure tank.

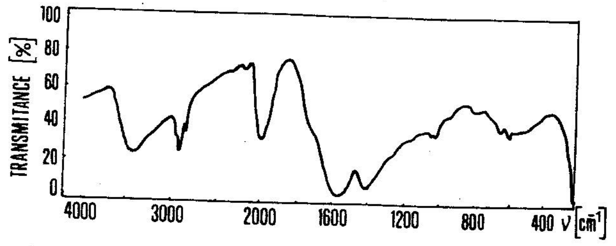


Fig. 10. IR absorption spectrum of the solid deposit on the wire in the case of the positive corona discharge.

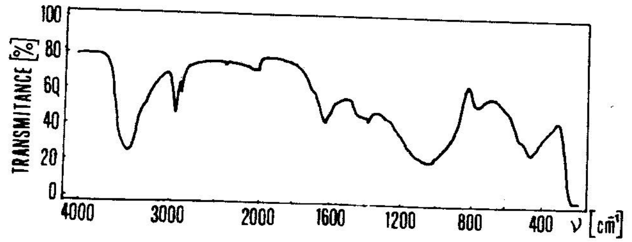


Fig. 11. IR absorption spectrum of the solid deposit in the wire in the case of the negative corona discharge.

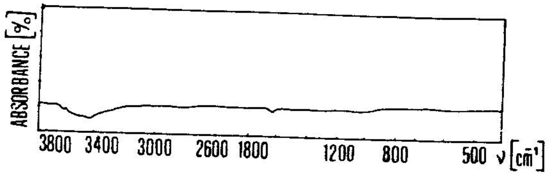


Fig. 12. IR absorption spectrum of pure activated carbon.

These spectra are shown in Fig. 10 (the case of the positive corona discharge) and in Fig. 11 (the case of the negative corona discharge). The IR absorption spectrum of pure activated carbon was also taken for comparison and is presented in Fig. 12.

## III. DISCUSSION

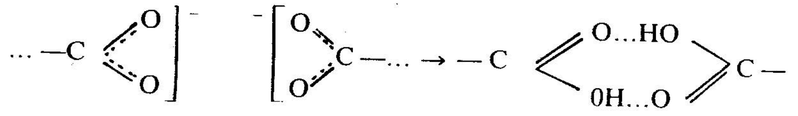
The sample of the dark deposit isolated from the central electrode was in both cases of a polymeric nature (the absorption bands are wider and more diffused).

The IR absorption spectrum of the solid sample formed in the case of the positive corona discharge has these absorption bands:

520 cm$^{-1}$ — ?
570 cm$^{-1}$ — ?
610 cm$^{-1}$ — deformation wagging vibration of a carboxylate ion
660 cm$^{-1}$ — deformation scissoring vibration of a carboxylate ion
790 cm$^{-1}$ — deformation vibration of a $CH_2$ group
940 cm$^{-1}$ — deformation vibration of a cyclic dimer of carboxylic acid
1025 cm$^{-1}$ —}
1045 cm$^{-1}$ —} symmetrical stretching vibration of an allene group
1160 cm$^{-1}$ — stretching vibration of a group C—O—C
1410 cm$^{-1}$ — symmetrical stretching vibration of a carboxylate ion
1570 cm$^{-1}$ — antisymmetrical stretching vibration of a carbixylate ion
1580—1640 cm$^{-1}$ — stretching vibration of conjugated carbon — carbon double bonds
2000 cm$^{-1}$ — antisymmetrical stretching vibration of an allene group
2190 cm$^{-1}$ — stretching vibration of carbon-carbon triple bonds
2850 cm$^{-1}$ —}
2920 cm$^{-1}$ —} stretching vibration of a $CH_2$ group
3420 cm$^{-1}$ — stretching vibration of a cycle dimer of carboxylic (2400—3600) acid.

These absorption bands yield the following structural units:

1) more than five conjugated carbon-carbon double bonds with an open chain;
2) an allene group;
3) a triple carbon-carbon bond;
4) a bond system C—O—C;
5) the open chain ends with the carboxylate ion, which reacts with the water (ultimate pressure was about 1 Pa). This yields the formation of the dimer observed according to the following scheme:



We can conclude that the deposit on the inside electrode is a mixture of dimers and polymers of different types. This effect can be practically explained by the non-monoenergetical distribution of electrons in the ionization zone.

The sample isolated in the case of a negative corona discharge does not create a continuous deposit on the wire surface but only small spots. The IR absorption spectrum obtained in this case yields the following absorption bands:

| | |
|---|---|
| 465 $cm^{-1}$ — | stretching vibration of an OH group bonded on metals |
| 765 $cm^{-1}$ — | deformation vibration of a $CH_2$ group<br>stretching vibration of a $CO_3^-$ ion |
| 1040 $cm^{-1}$ — | stretching vibration of primar alcohols (group C—OH)<br>deformation vibration of an OH group<br>stretching vibration of ozone compounds |
| 1380 $cm^{-1}$ — | deformation vibration of groups $CH_2$; $CH_2$—CO |
| 1410 $cm^{-1}$ — | stretching vibration of a $CO_3^-$ ion<br>symmetrical stretching vibration of a carboxylate ion |
| 1630 $cm^{-1}$ — | antisymmetrical stretching vibration of a carboxylate ion<br>stretching vibration of conjugated carbon-carbon double bonds |
| 2850 $cm^{-1}$ —<br>2920 $cm^{-1}$ — | stretching vibration of a $CH_2$ group |
| 3440 $cm^{-1}$ — | stretching vibration of an OH group. |

From absorption bands described and from the discharge behaviour we have deduced the following structure of the deposit:

The essential building units consist of more than five conjugated carbon-carbon double bonds. Such a chain ends with the carboxylate ion, which dimerized in the same way as in the case of a positive corona discharge. From loosened oxygen ozone is formed. The presence of water (ultimate pressure was about 1 Pa) was responsible for the forming of alcohols and $CH_2$ groups.

The early change of the corona discharge mode to the other form and the rapid heating of the inside electrode connected with this change stimulated the formation of compounds containing metal atoms (ozone compounds, alcohols).

In both the positive and the negative corona the following important phenomenon was observed. The corona discharge destroyed the molecule of CO and made the forming of compounds possible which did not contain the carbon-oxygen double bond at all (there are no peaks in the 2100—2200 $cm^{-1}$ and 1700 $cm^{-1}$ region). The interpretation of spectra was made with the aid of literature [2, 3, 4, 5, 6, 7, 8].

Comparing the IR spectra of gaseous products in both cases (Figs. 6, 7, 8) and the reference IR spectrum of CO from the pressure tank (Fig. 9) it follows that no gaseous products are formed in a sufficient concentration. The CO supplied in the pressure tank is contaminated. The absorption bands of the contaminating material have the vawe numbers in the KBr region 620 $cm^{-1}$, 645 $cm^{-1}$, in the LiF region 2010 $cm^{-1}$, 2030 $cm^{-1}$. The characteristic bands 2010 and 2030 $cm^{-1}$ are responsible for the stretching vibration of C≡O bands of metal carbonyl compounds. The deformation vibration bands at the wave numbers 620 and 645 $cm^{-1}$ correspond probably to $Fe(CO)_5$, where the bonds between C and O of all the five carbonyl groups are of the C≡O type. This compound quite easily passed through the liquid nitrogen trap when the introducing rate of CO was too quick. Owing to the fact that the extinction coefficients of $Fe(CO)_5$ in the metal carbonyl region are very high, also small amounts of this compound can be detected.

The presence of gaseous reaction products was also tested by mass spectrometry. Besides peaks corresponding to the mass numbers 12($C^+$), 14($CO^{++}$), 16($O^+$), 28($CO^+$) no other peaks were observed. At that time we did not know about the existence of $Fe(CO)_5$ in the pressure tank, and therefore the mass spectrum was scanned only in the region from 1 to 100 u.

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