of these samples ϕ increased to values exceeding unity.

These irregularities were traced to retention of carbon monoxide by solid carbonyl sulfide at liquid air temperature. After suitable modification of the apparatus, most of this retained gas could be recovered in successive portions and measured. Thus corrected, ϕ became 0.9 approximately. Further corrected by means of a reasonable estimate of the traces of gas still retained, ϕ was very close to unity.

This outcome corresponds to the equation $COS + h\nu = CO + S$, in which the states of the products cannot at present be exactly specified. Apparently, recombination of the primary products, and other secondary reactions involving carbon monoxide are negligible.

[CONTRIBUTION FROM CARNEGIE INSTITUTE OF TECHNOLOGY]

Studies on Cellulose Compounds

BY E. BERL AND W. KOERBER

The reason for the solution of cellulose esters and ethers in certain solvents has not been discussed very thoroughly up to this time. With the exception of the publications of Highfield[1] and Werner and Engelmann[2] very little material has been published.

It seems that cellulose nitrates are soluble at room temperature in those solvents which have partial valences on oxygen, for example, in ketones like acetone. Completely substituted cellulose triacetates are soluble at room temperature in solvents which, like chloroform or dichloromethane, have partial valences on the carbon. If, besides the bound acetyl groups, unsubstituted OH groups are present in a certain ratio, the solution in ketones with partial valences on the carbonyl oxygen takes place at room temperature.

The influence of temperature on the solubility of cellulose esters has been studied very little. In this publication the solubility of different cellulose nitrates and acetates in fibrous form in different solvents at room temperature and at $-50°$ has been studied. The microphotographs (Figs. 1a, 1b, 1c) which are made with an enlargement of ×436 show the results. The solubility Tables I and II are self-explanatory.

One hundred mg. samples dried over calcium chloride were put into test-tubes and 2 cc. of the organic solvent added. The tubes were kept in a water-bath at 20° for fifteen minutes. Another series of test-tubes with the same samples and solvents was kept in solid carbon dioxide at −50° for fifteen minutes.

The materials were stained with oil red (Du Pont Company) in carbon tetrachloride solution. Before stain-

ing, all materials were dried at 100°, then stained on the slide, and dried again.

The effects of the solvents on the materials at the different temperatures are shown in Tables I and II: −, fibers remain insoluble and unchanged; +, fibers have lost their original structure, and form a solid, translucent lump of the same refractive index as the solvent; ++, fibers form a gel at low temperature which consists of small, soft, translucent lumps. This gel does not change its consistency when warmed to room temperature. It is highly swollen and has a limited solubility in the solvent. After standing for a while at room temperature two phases are formed: the viscous gel covered by the nonviscous solvent; +++, fibers are completely dissolved, the viscosity of the solvent is increased; (+) the width of the fibers has been considerably enlarged by swelling.

TABLE I
SOLUBILITY OF CELLULOSE NITRATES

Solvents	°C.	12.02%	12.6%	13.4%	13.9%
Ether	+20	−(2)	−(7)	−(2)	−(30)
	−50	−(3)	−(8)	−(22)	−(31)
Ethanol	+20	−(4)	−(9)	−(23)	−(32)
	−50	++(5)	−(10)	−(24)	−(33)
Ether–ethanol	+20	+++	+++	−	−(28)
60:40	−50	+++	+++	++(15)	+(29)
Methanol	+20	+++	+++	−	−(34)
	−50	+++	+++	−(25)	++(35)
Glacial acetic acid	+20	+++	+++	++(26)	
	+20	+++	+++	−(20)	−
Ethylene glycol	+20	−	−	−	−
Acetic anhydride	+20	+++	++	++	++
Formic acid	+20	−	−	−	−
Ethyl acetate	+20	+++	+++	+++	+++
Methyl acetate	+20	+++	+++	(+)	(+)
	−50	+++	+++	+++	+++

TABLE II
SOLUBILITY OF CELLULOSE TRIACETATE

	+20°	−50°
Acetone	−(37)	++(38)
Methyl acetate	−(39)	(+)(40)

The ratios of ether to ethanol in the experiments with cellulose nitrates were varied considerably. Besides the normal mixture of ether to ethanol (2:1) three other

(1) Highfield, Trans. Faraday Soc., 22, 57 (1926).

(2) Werner and Engelmann, Z. angew. Chem., 42, 437 (1929).

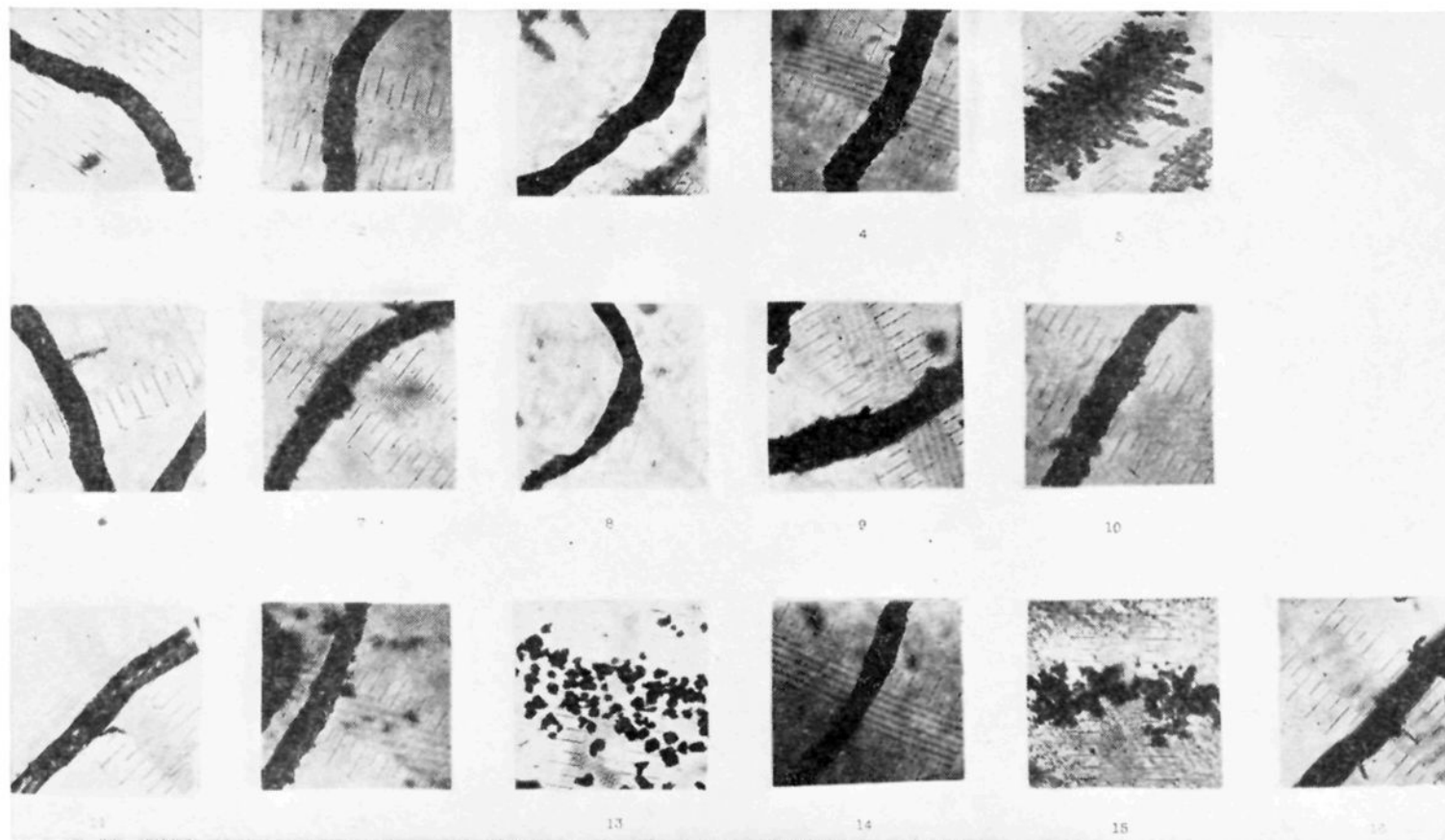Fig. 1a.—×436 microphotographs of fibers in various solvents.

1. Nitrate (12.02%).
2. Same in ether at +20°.
3. Same in ether at −50°.
4. Same in ethanol at +20°.
5. Same in ethanol at −50°.
6. Nitrate (12.6%).
7. Same in ether at +20°.
8. Same in ether at −50°.
9. Same in ethanol at +20°.
10. Same in ethanol at −50°.
11. Nitrate (13.4%).
12. Same in ether-ethanol (80:20) at +20°.
13. Same at −50°.
14. Same (60:40) at +20°.
15. Same at −50°.
16. Same (40:60) at +20°.

mixtures, 4:1, and 2:3, and 1:4 were used. The complete solubility of cellulose nitrates with 12.02% nitrogen and 12.6% nitrogen in ether–ethanol with different ratios between ether and ethanol at room temperature and at −50° was expected. Two highly nitrated esters with 13.4 and 13.9% bound nitrogen (gun cotton) were practically insoluble in the different mixtures of ether and ethanol at room temperature. A slight swelling effect was observed. At −50° all the fibers disintegrated in these ether–ethanol mixtures, as can be seen from Nos. 13, 15, 17, and 19, independent of the low or high nitrogen content of the gun cotton.

A similar effect of strong disintegration was observed by using ethanol alone as a solvent at −50° with cellulose nitrate with 12.02% nitrogen content (No. 5). The pyro quality with 12.6% nitrogen and the gun cottons did not show a similar effect with ethanol alone at −50° (No. 10).

These experiments seem to give an explanation for the peculiar solvent action of mixtures of ether and ethanol. Experiments on a very large scale have shown that in mixing ethyl ether and ethanol no change in temperature and no contraction or expansion takes place. Therefore, it can be established that ethyl ether and ethanol do not form molecular compounds. It is probable that a molecular compound between these lower nitrated (10.0–12.7% N) cellulose nitrates and ethanol is formed which is soluble in ether. If enough unsubstituted OH groups are present, as is the case in the material with 12.02% nitrogen, then at −50° a strong disintegration in ethanol is observed

(No. 5). At room temperature this molecular compound is dissociated, therefore, only a swelling effect (No. 4) is observed. The materials with 12.6 and more per cent. of nitrogen have not enough free OH groups, so that this effect at −50° does not take place (Nos. 9, 10, 23, 24, 32, 33). From the experiments it can be seen that ether alone has practically no dissolving effect on any cellulose nitrate at room temperature and at −50° (Nos. 2, 3, 7, 8, 21, 22, 30, 31). The theory that an oxonium compound between ether and cellulose nitrate is formed, which is ethanol soluble, is not substantiated by these experiments.

It is known that methanol alone has a strong swelling and dissolving action on lower nitrated cellulose nitrates. Material with 13.4 and 13.9% bound nitrogen, according to Nos. 25 and 34, shows a slight swelling effect on the fibers at room temperature. At −50° the complete solution of medium and highly nitrated gun cotton was observed (Nos. 26 and 35).

The solubility of cellulose nitrates in glacial acetic acid seems to go parallel with the solubility in ether–ethanol. Lower nitrated collodion wools and pyro qualities are soluble. Gun cotton (No. 20) swells slightly but is insoluble.

All cellulose nitrates are soluble at room temperature in acetic anhydride. The lowest nitrated material with 12.02% nitrogen content shows the best solubility. It is remarkable that formic acid (85% HCOOH) does not dissolve cellulose nitrates, this in contrast to cellulose acetates which show a much better solubility in formic acid than in glacial acetic acid.
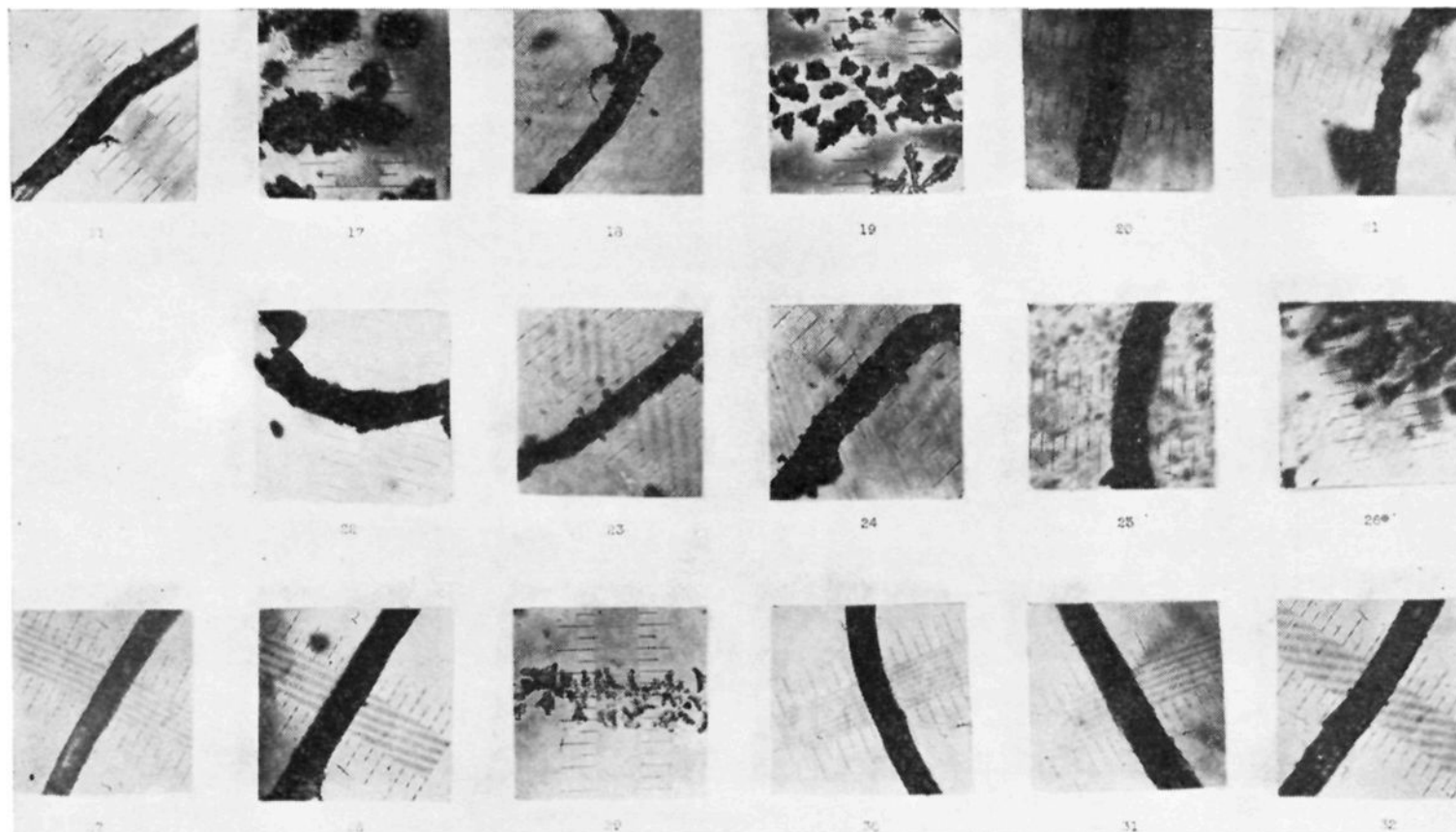
Fig. 1b.—×436 microphotographs of fibers in various solvents.

11. Nitrate (13.4%).
17. Same in ether-ethanol (40:60) at −50°.
18. Same (20:80) at +20°.
19. Same at −50°.
20. Same in glacial acetic acid at +20°.

21. Same in ether at +20°.
22. Same at −50°.
23. Same in ethanol at +20°.
24. Same at −50°.
25. Same in methanol at +20°.
26. Same at −50°.
27. Nitrate (13.9%).

28. Same in ether-ethanol (60:40) at +20°.
29. Same at −50°.
30. Same in ether at +20°.
31. Same at −50°.
32. Same in ethanol at +20°.
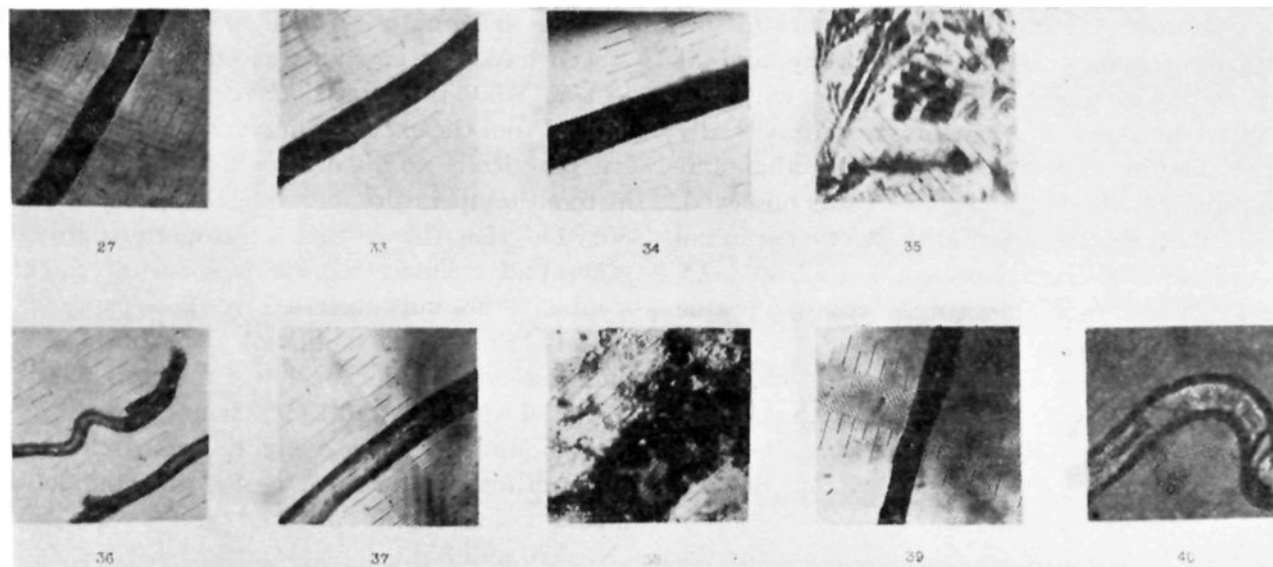
Fig. 1c.—×436 microphotographs of fibers in various solvents.

27. Nitrate (13.9%).
33. Same in ethanol at −50°.
34. Same in methanol at +20°.
35. Same at −50°.

36. Triacetate.
37. Same in acetone at +20°.
38. Same at −50°.
39. Same in methyl acetate at +20°.
40. Same at −50°.

Ethyl acetate is an excellent solvent for all cellulose nitrates independent of their nitrogen content.

Methyl acetate is an excellent solvent at room temperature for the collodion wools with 12.02 and 12.6% nitro-gen. It swells the gun cottons with 13.4 and 13.9% nitrogen, but does not dissolve them at room temperature. It is an excellent solvent for all cellulose nitrates at −50°.

Cellulose triacetate with 62.2% bound acetic acid swells

but does not dissolve in acetone (compare No. 37 with 36). This solvent completely disintegrates cellulose triacetate at −50° (No. 38).

Methyl acetate swells the cellulose triacetate fibers at −50° (No. 40) much more than at room temperature (No. 39).

Solutions (1:1000) of materials insoluble in a solvent or solvent mixture at room temperature, but completely soluble at low temperature, show the formation of finely divided, swollen particles by increasing the temperature from −50 to −20 or to −10°.

The solution of an ester or ether of cellulose in a solvent is preceded by a swelling effect and the development of heat. The influence of lower temperatures on this swelling and solution effect can be explained by the formation of soluble molecular compounds which dissociate at higher temperatures. The exothermic character of swelling reactions also works in the direction of an increased solubility at low temperatures.

It is known that certain mono alkyl derivatives of cellulose dissolve in water at room temperature and become insoluble in boiling water. Here also a molecular compound is formed between the unsubstituted OH groups containing monoalkylcellulose and water. This molecular compound is soluble in water at room temperature. At higher temperatures this molecular compound dissociates; the alkylcellulose, therefore, becomes insoluble in hot water.

Summary

Cellulose esters insoluble in certain solvents or solvent mixtures at room temperature may become soluble at lower temperatures (−50°). This can be explained by the formation of soluble molecular compounds, which dissociate at elevated temperatures, and by the exothermic character of the swelling reactions.

Carcinogenic Hydrocarbons. III. 20-Isopropylcholanthrene. A Comparison of the Fluorescence and Crystal Forms of Methylcholanthrene, Ethylcholanthrene and Isopropylcholanthrene[1,2]

BY WILLIAM F. BRUCE AND FLOYD TODD

Cholanthrene and its 20-methyl derivative are particularly interesting carcinogenic hydrocarbons because they are among the most active cancer producing materials.[3] The 20-t-butyl member of this group of substituted cholanthrenes has been prepared,[4] and more recently the 20-ethyl homolog has been reported.[1] The present paper describes the preparation of the 20-isopropyl member of this series. In addition, the fluorescence of the methyl, ethyl and isopropyl members under comparable conditions has been measured. A detailed description of the crystal properties of these three substances is included in the experimental part, having been determined microscopically by Professor C. W. Mason, to whom we give hearty thanks for his collaboration.

A comparison of the fluorescence of these three cholanthrene derivatives shows that the intensity of fluorescence, measured under comparable conditions, is strongest for the methyl and weakest for the isopropyl member. From the data now available for this series, fluorescence and carcinogenic activity appear to be roughly parallel. A more extensive comparison will be available when the series is completed.

Study of the crystal form of 20-methyl, ethyl and isopropyl cholanthrenes shows that the methyl derivative has two forms.[5] The most common form is acicular, belonging to the triclinic system. Above approximately 140°, however, a platelet or monoclinic form is more stable. Since the conversion of one form to the other is not rapid, it is possible by rapid cooling to secure chiefly the platelet form. This is particularly easy in n-propyl alcohol, as Bachmann has pointed out. From a concentrated benzene solution by rapid cooling, both forms can be obtained together. The ethyl and isopropyl members of this group have been observed in only a plate-like form. The crystal system differs, however, for the former has been assigned to the monoclinic system and the latter to the orthorhombic. The characteristic constants for these substances are included in the experimental part.

The preparation of isopropylcholanthrene was accomplished by the general synthesis of Fieser and Seligman, with modifications like those made

(1) Preceding paper, Bruce and Kahn, THIS JOURNAL, **60**, 1017–1019 (1938).

(2) Taken in part from the Thesis of Floyd Todd submitted in partial fulfilment of the requirements for the degree of M.S. at Cornell University.

(3) For a recent survey of the literature see Fieser, *Am. J. Cancer*, **34**, 37–124 (1938).

(4) Fieser and Snow, THIS JOURNAL, **60**, 176 (1938).

(5) *Cf.* Bachmann, *J. Org. Chem.*, **1**, 352 (1936).