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On the Preparation of UV Transparent, Saturated Hydrocarbons

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After treatment with fuming sulfuric acid and alkali, samples of isopentane, 3-methylpentane, hexane and cyclohexane were distilled in vacuum at a very high rate, 200 ml per minute. The first fractions were found to contain only dissolved oxygen as main absorbing impurity. By degassing in vacuum at 77°K the residual absorption at 25°C was always found to be less than 0.01 at 220 mμ (1 cm path length). At 200 mμ the absorption varied from about 0.005, isopentane, to about 0.05, cyclohexane. Repetition of the procedure resulted in still lower absorptions. These absorptions seem to be the lowest ever reported for any hydrocarbon.

Photolysis to constant spectrum of hydrocarbon samples with different oxygen contents indicated that the completely pure hydrocarbon should have no significant absorption down to 200 mμ. The purity of the hydrocarbons was further estimated from the spectral behavior of dissolved iodine, especially at 77°K.

During low temperature photolysis studies of organic disulfides and mercaptans dissolved in glasses of mixed hydrocarbons, great changes were sometimes observed in the UV spectral behavior of the solvent itself.[1] The mere freezing down of iodine in the same kind of hydrocarbon mixtures frequently resulted in different spectra with different hydrocarbon samples, and as a result in different photochemical behavior.[2,3] A systematic study was therefore undertaken to find out if these phenomena could be caused by the presence of impurities difficult to remove.

The hydrocarbons were subjected to purification in a number of ways, *e.g.* fractional distillation, absorption with activated silica gel and/or molecular sieves, selective photolysis followed by treatment with sulfuric acid, etc. During this work it became apparent that more or less firmly bound oxygen is responsible for many discrepancies observed in the UV absorption spectra around 50 kK (*K*ilo *K*ayser = 1000 cm^{-1}).** Based on this idea a new simplified purification procedure was developed.

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** This subject will be dealt with in a later publication.

EXPERIMENTAL

The purification method. The hydrocarbon (1.5 litre, technical or c.p. grade) was first shaken with fuming sulfuric acid until the benzene spectrum [4] completely vanished.* Sulfur dioxide was extracted by dilute alkali, and an important absorption peak at 48 kK [6] was removed by shaking with alkali pellets.[7,8] Shaking was necessary, at least in the case of the higher boiling hydrocarbons, because the removal of the absorption was connected with the formation of a white precipitate on the pellets.[9]

If a hydrocarbon free from isomers *etc.* was required a normal fractional distillation followed, using an all pyrex column (45 theoretical plates). Sometimes, however, the main fractions of the hydrocarbon showed new high and characteristic absorption bands (they were absent in the substance remaining in the still pot) which could be removed by distilling through a short column with molecular sieves (4A or 5A), kept a few degrees above the condensation point of the hydrocarbon. Extraction with sulfuric acid usually served the same purpose.

If the aim was only to prepare a u.v. transparent hydrocarbon solvent, the fractional distillation could be excluded.

At this stage of the purification process the hydrocarbon samples showed a varying absorption between 40 and 50 kK, even after repeated crystallizations in vacuum at 77°K. The following procedure, however, led to a striking decrease in this absorption. (The 48 kK band is not affected by this treatment.)

The hydrocarbon (1.5 litre) was gently shaken for half an hour with sulfuric acid. About 1/10 to 1/5 of the solvent (*i.e.* 150—300 ml) was then distilled off in vacuum in about one minute, which was practically the same time that air was present in concentrations large enough to maintain stable boiling. The receiver was cooled with liquid nitrogen. After drying with alkali pellets this fraction contained only physically dissolved oxygen as main absorbing impurity. A simple degassing, best performed by freezing of the hydrocarbon in vacuum at 77°K, removed the oxygen. After this treatment all the hydrocarbons investigated showed a residual absorption (1 cm path length, 25°C) of less than 0.01 at 45 kK.[10] At 50 kK it varied from about 0.005, in the case of isopentane, to about 0.05, in the case of cyclohexane,[10] 3-methylpentane and hexane showing absorptions between these values.

A repetition once or twice of the complete purification process (starting with fuming sulfuric acid) yielded 3-methylpentane of the same low residual absorption as isopentane. Cyclohexane was much more difficult to purify, as a repetition of the purification procedure did not lead to a further satisfactory decrease in absorption.

Continued distillation of more hydrocarbon from the residual bulk of the hydrocarbon sample after the quick distillation yielded fractions with increased residual absorptions. To increase the yield of pure sample those later fractions (up to *ca.* 50 % of the total amount) were recycled, starting with the treatment with sulfuric acid.

The spectrophotometric measurements were carried out with a Unicam SP 700 recording spectrophotometer, equipped with a plastic insulated cell compartment [11] designed for low temperature measurements with modified cells (Fig. 1). The branch with the ampoule (A), containing, *e.g.*, iodine, and the Pyrex hammer (B) were first sealed (C) to the cell. Then the hydrocarbon was introduced into the 30 ml bulb (D), often together with appropriate chemicals, *e.g.* Na_2CO_3, KOH, H_2SO_4, $LiAlH_4$, *etc.* The degassing was achieved by dipping the bulb into liquid nitrogen while evacuating, alternating with warming to room temperature with the evacuation stop-cock closed. If the bulb was filled to less than half its volume there was no risk of cracking due to an occasionally occurring sudden crystallization. The cell was sealed off (E), and the hydrocarbon was distilled or decanted into the optical part (F) of the cell before use.

When the solute, *e.g.* iodine, was to be introduced, the whole cell was first frozen down, and the thin walled ampoule tip was then broken by shaking. The location of the

* When 3-methylpentane, free from the 2-isomer was required shaking was unfavorable, as sulfuric acid catalyzes isomerization.[5] In this case the hydrocarbon was left for a few days in contact with the acid.

ampoule close to the optical part of the cell permitted direct dipping into liquid nitrogen without further transfer of substance between different parts of the cell system.

The absorption measurements were made against air as a reference. The net absorption (E) was calculated as the difference between the recorded curve of the filled cell and a zero line almost parallel below the curve of the same empty cell. The almost constant difference between the recorded curve of the empty cell and the zero line actually used was due to the difference in reflexion between the empty and the filled cells. In wave length regions where the solvents did not absorb, this difference could be measured directly. Thus in the visible, where even the quartz cells were completely transparent, the recorded values of the filled cells were about half those of the empty cells, *i.e.* the recorded differences were about 0.030 absorption units. At 40 kK, where the cells exhibited important absorption, the recorded differences were always somewhat smaller, about 0.025 (for almost any nonabsorbing solvent). At 50 kK, where the influence of the absorption of the solvents made direct measurements impossible, the differences were estimated to be about 0.020 (*cf.* below).

The photolysis experiments were performed by using air cooled, Philips SP 900 W, high pressure mercury lamps, placed one on each side of the cell at a distance of about 20 cm from the cell. The light was filtered by 3.5 cm of circulating $NiSO_4$ solution, 285 g $NiSO_4 \cdot 6\ H_2O$ per litre,[12] giving a high wave number cut off limit at about 45.5 kK. For further details see Ref. 13.

Purity control by photolysis. If a highly purified hydrocarbon sample was not completely degassed, the absorption was found to be proportional to the oxygen concentration.[10,14] A few minutes photolysis of such a sample generally led to relatively small changes in the absorption spectrum.[15] Continued photolysis, however, soon gave a manifold increase in absorption at 50 kK, and a decrease below 45 kK. Finally, after 2—12 h of photolysis, a constant spectrum, starting above 45.5 kK, was reached, the faster the greater the initial absorption. When the recorded final absorptions A_∞ were plotted against the starting absorptions A_0 for the different samples straight lines were obtained for wave lengths in the region 48 to 50 kK. A reasonable assumption should be that $A_\infty - A_h = k(A_0 - A_h)$, where A_h is the unknown absorption with an oxygen-free hydrocarbon

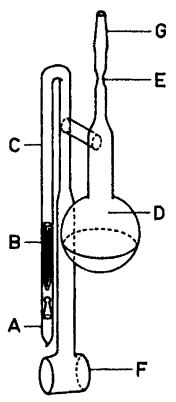

Fig. 1. Total view of modified cell. A. Ampoule with solute. B. Pyrex hammer. C. Connecting point of the ampoule branch. D. 30 ml bulb with solvent. E. Sealing off point. F. Optical part (all quartz). G. Joint to the vacuum line.

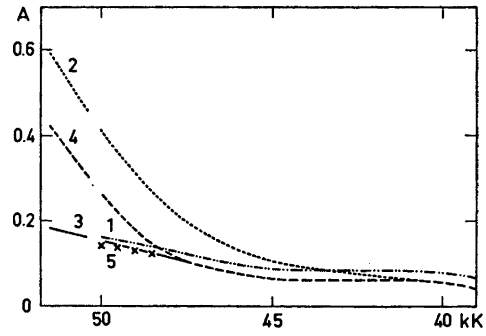

Fig. 2. Registered absorption (A) as a function of $1/\lambda$ (in kK). Cell length: 2 cm. Reference: air. Temperature: 25°C. (1) Empty cell. (2) Cell filled with isopentane in contact with air. (3) Ditto, evacuated and (4) thereafter photolyzed to constant spectrum (12 h). (5) Extrapolated values (A_h) for oxygen-free hydrocarbon. (Equivalent to zero line.)

sample in the cell, and k is a proportionality constant. Rearrangement gives $A_\infty = kA_0 + (1 - k)A_h$, an expression that was identified with the straight lines above. The A_h-values then obtained were found to fit a curve lying almost parallel below the recorded curve of the empty cell (Fig. 2). At 50 kK the difference between the curves was still as high as 0.020 absorption units indicating that the absorption of the oxygenfree hydrocarbon was neglible in this region.

Calculations with ordinary molar extinction coefficients of dissolved oxygen [10,16] give that the lowest solvent absorptions obtained in this work correspond to oxygen concentrations in the order of 10^{-5} moles/litre. The approximately ten fold increase in absorption at 50 kK, obtained above upon photolysis to constant spectrum, may also be used for estimations of low oxygen concentrations. Such photolysis, in combination with extraction of the photolysis products with sulfuric acid, will of course give low absorbing solvents with still lower oxygen contents.

Purity control using iodine. Slow freezing down to 77°K of iodine in mixtures of hydrocarbons, purified in the way described above, generally resulted in the crystallization of iodine, even at concentrations as low as 10^{-5} moles/litre. This was in good agreement with freezing down experiments with iodine in mixtures of hydrocarbons, purified through normal fractional distillation, followed by adsorption on silica gel.[17,4,2] The degree and nature of crystallization could be seen from the nonspecific background absorption below 40 kK at 77°K (*cf.* Ref. 3). The center of this absorption appeared at longer wave lengths under conditions favouring the growth of crystallites: slow cooling, increased rate of diffusion by increase in temperature above the melting region of the matrix, and use of solvents of low viscosity.[18]

At low concentrations rapid freezing down generally led to super cooling: no Tyndall-effect or background absorption was observed. Both appeared, however, during warm up. This super cooling was very easily achieved in pure 3-methylpentane (containing about 1 % 2-methylpentane), which was the most viscous solvent investigated. As can be seen from Fig. 3 this solution did not show the ordinary displacement of the long wave length absorption peak from 19 to about 22 kK [17,3] either upon freezing down, or during warm up. The number of freezing down experiments with pure isopentane were few because of sudden solvent crystallization that damaged both the cell and the cell compartment.

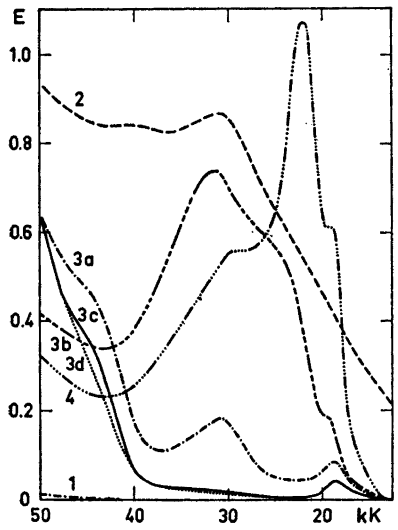

Fig. 3. Low temperature spectra of iodine solution. Cell length: 2 cm. (1) Purified hydrocarbon after evacuation at room temperature. (2) 2×10^{-5} M iodine in isopentane (containing 1 % pentane and traces of water) at 77°K. Fast freezing. (3) 2×10^{-5} M iodine in 3-methylpentane (containing 1 % 2-methylpentane) (a) at 77°K. Slower freezing. (b) after 50 min warm up when the temperature had reached 100°K. Cloudy. (c) after 90 min warm up; temperature 170°K. Clear. (d) at room temperature. (4) 2×10^{-5} M iodine in the same 3-methylpentane which had been degassed in vacuum at 77°K in contact with sulfuric acid. Frozen down to 77°K by direct immersion into liquid nitrogen. Cloudy.

In all cases super cooling could be prevented, if the outgassing was performed with the solvent in contact with sulfuric acid in the bulb. The iodine then always crystallized, even when the solution was cooled as rapidly as possible by direct immersion of the cell into liquid nitrogen. The spectrum (curve 4 in Fig. 3) then resembled very much the spectrum obtained upon slow freezing down, without the H_2SO_4 treatment (Ref. 3, Fig. 3). The same type of spectrum was also obtained by Timm [2] with hydrocarbons purified repeatedly in the way described by Potts [6] and Rosengren.[18] It seems to be representative of the spectral behavior of iodine in very pure hydrocarbons.

COMMENTS

The possibility of preparing solvents that are practically nonabsorbing in a broad wave length region has definite advantages. Differences in solvent absorption between sample cell and reference cell are eliminated. The solvent zero line obtained with the *one* cell technique described above will most probably be unchanged, as long as oxidizing solutes are not introduced. With isopentane and 3-methylpentane there was no detectable temperature dependence of solvent absorption in the temperature region extending from the boiling point of the solvent down to at least 0°C. It is true that at lower temperatures the spectral properties can be influenced by the possible precipitation of traces of water, but by proper drying, (*e.g.* with $LiAlH_4$ in the cell bulb), the same low solvent absorption can be maintained even at 77°K.

The fact that low absorption at 50 kK must be equivalent to low oxygen content [19,20] makes these solvents suitable for investigation of systems, that are sensitive to oxygen. In spectroscopy the perturbation due to oxygen may appear as enhancement of singlet-triplet transitions, quenching of phosphorescence, and charge-transfer to oxygen. A systematic investigation of these effects was not undertaken.

Another advantage of using low absorbing hydrocarbons is that they are highly resistant towards photolysis (*cf.* curves 3 and 4 in Fig. 2). The range of the photolyzing light can be extended to higher frequencies without interference from the solvent. It is best illustrated by the photolysis of iodine in mixtures of isopentane and 3-methylpentane, presented by Timm.[3] Low UV absorption up to 50 kK also seems to show the absence of impurities that can form strongly absorbing complexes with iodine upon freezing down. High absorption on the other hand does not necessarily mean that such complexes are formed. Thus many fractions from the quick distillation did not show any sign of strong complex formation with iodine upon *immediate* freezing down (*cf.* Ref. 3), even if they exhibited residual absorption in the order of 0.1 at 50 kK after the degassing.

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REFERENCES

1. Rosengren, Kj. *Acta Chem. Scand.* **16** (1962) 1418.
2. Timm, D. *Acta Chem. Scand.* **16** (1962) 1455.
3. Timm, D. *Acta Chem. Scand.* **20** (1966) 2219.
4. Sowden, R. G. and Davidson, N. *J. Am. Chem. Soc.* **78** (1956) 1291.

5. Burwell, R. L., Scott, R. B., Maury, L. G. and Hussey, A. S. *J. Am. Chem. Soc.* **76** (1954) 5822.
6. Potts, W. J. *J. Chem. Phys.* **20** (1952) 809.
7. Porter, G. *Proc. Roy. Soc.* **A 262** (1961) 476.
8. Hesse, G. and Schildknecht, H. *Angew. Chem.* **67** (1955) 737.
9. *Cf.* Grafstein, D. *Anal. Chem.* **26** (1954) 523.
10. *Cf.* Munck, A. U. and Scott, J. F. *Nature* **177** (1956) 587.
11. Rosengren, Kj., Sunner, S. and Timm, D. *Acta Chem. Scand.* **16** (1962) 467.
12. Kasha, M. *J. Opt. Soc. Am.* **38** (1948) 929.
13. Rosengren, Kj., Sunner, S. and Timm, D. *Acta Chem. Scand.* **16** (1962) 495.
14. Jortner, J. and Sokolov, S. *J. Phys. Chem.* **65** (1961) 1633.
15. Maclean, M. E., Jencks, P. J. and Acree, S. F. *J. Res. Natl. Bur. Std.* **34** (1945) 271.
16. Heidt, L. J. and Johnson, A. M. *J. Am. Chem. Soc.* **79** (1957) 5587.
17. Ham, J. S. *J. Am. Chem. Soc.* **76** (1954) 3875.
18. Rosengren, Kj. *Acta Chem. Scand.* **16** (1962) 1421.
19. Evans, D. F. *J. Chem. Soc.* **1957** 1351.
20. Tsubomura, H. and Mulliken, R. S. *J. Am. Chem. Soc.* **82** (1960) 5966.

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