The Identification and Relative Retention Times of p,p′-Kelthane and its Breakdown Product p,p′-Dichlorobenzophenone Using GLC

by NORMAN L. MORGAN
California Department of Agriculture
State of California
Sacramento, California

During the past year there has been a growing concern over the identification of those peaks obtained by the injection of p,p'-Kelthane into gas chromatographs. Some investigators have reported as many as seven peaks (1), while others have reported only one (2), or two peaks (3). This is due in part to the use of both a technical grade Kelthane and a purified p,p'-Kelthane. This investigation is concerned with only the pure p,p'-Kelthane.

Purified p,p'-Kelthane as received from Rohm & Haas was scanned on a Beckmann IR-4 and found to be 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol. This pure standard was injected into a Varian Autoprep Model 700-A Gas Chromatograph and two major peaks were obtained, as shown in Figure 1. The first

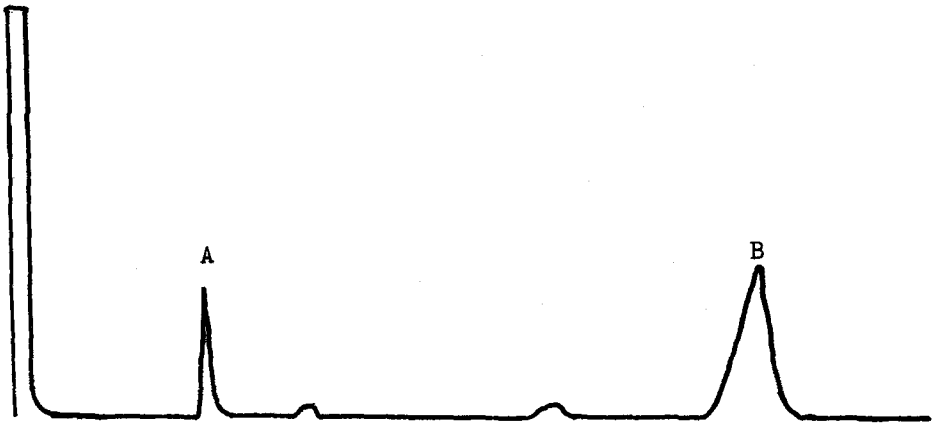

Fig. 1. Chromatogram of 300 micrograms of p,p'-Kelthane injected into a Varian Autoprep Model 700-A GLC with a ¼" by 6' SS column packed with 5% Dow 11, 60/80 mesh, DMCS treated Chromosorb W. Inj. Temp. 230°C., Col. Temp. 220°C., Det. Temp. 260°C. Flow rate 60 ml/min. He.

major peak, labeled A, with a retention time of 3.6 minutes, and a second major peak, labeled B, with a retention time of 13.8 minutes, were obtained. The two minor intermediate peaks are unidentified at this time.

Both peaks A and B were collected in sufficient quantity to analyze on the Beckmann IR-4. The infrared scans were made in CS_2, using a 5 mm pathlength cell.

The infrared spectrum of peak A, shown in Figure 2, was compared with that of pure recrystallized 4,4'-dichlorobenzophenone, shown in Figure 3, and the

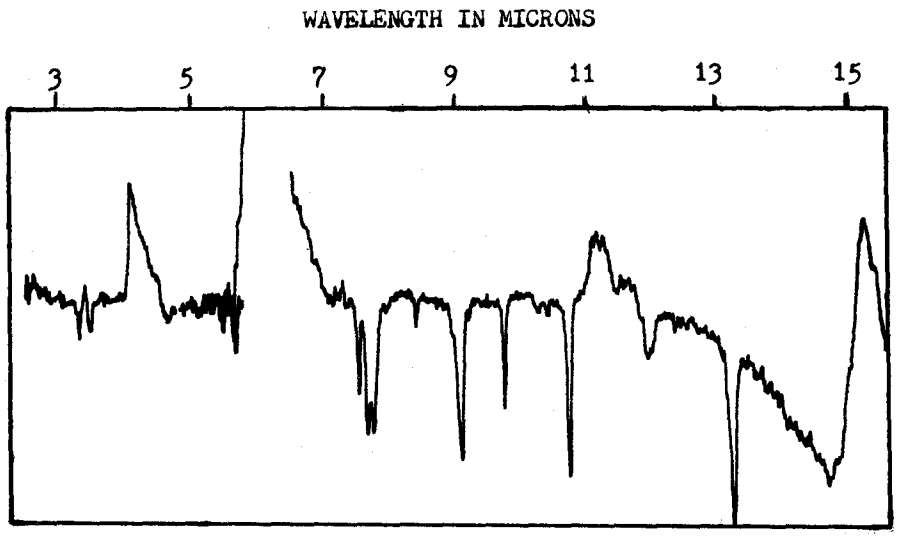

Fig. 2. Infra-red spectra of peak A collected from the Varian Autoprep Model 700-A GLC. 5 mm pathlength in CS_2.

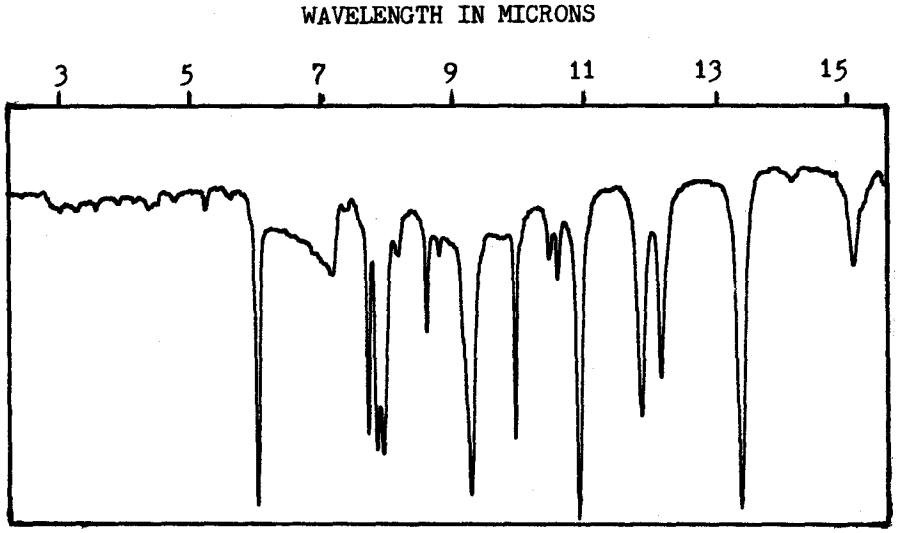

Fig. 3. Infra-red spectra of pure p,p'-dichlorobenzophenone. 1 mm pathlength in CS_2.

infrared spectrum of pure p,p'-Kelthane, Figure 5. The absence of the O-H stretch at 2.8 microns, and the presence of both the C=O stretch at 6.0 microns and the C-O stretch at 7.9 microns show that peak A is p,p'-dichlorobenzophenone and not p,p'-Kelthane as reported by some investigators (4).

The infrared spectrum of peak B, as shown in Figure 4, was compared with the infrared spectrum of pure p,p'-Kelthane, shown in Figure 5. The results show the absence of both the C=O and the C-O stretch and the presence of the O-H stretch. This indicates that peak B is <u>not</u> a breakdown product of p,p'-Kelthane, but p,p'-Kelthane itself.

Discussion

The amount of breakdown of p,p'-Kelthane to p,p'-dichlorobenzophenone varies with (a) the carrier gas used, and (b) the operating parameters of the GLC. When a 300 microgram sample of p,p'-Kelthane was injected into the Autoprep, using Helium carrier gas, Figure 1, and compared to a chromatogram of 5 micrograms of the same p,p'-Kelthane injected into a Dohrmann Model 100 Gas Chromatograph, using Nitrogen carrier gas, Figure 6, the breakdown differences became apparent. In Figure 6, the first peak, with a retention time of 4.5 minutes is p,p'-dichloro-

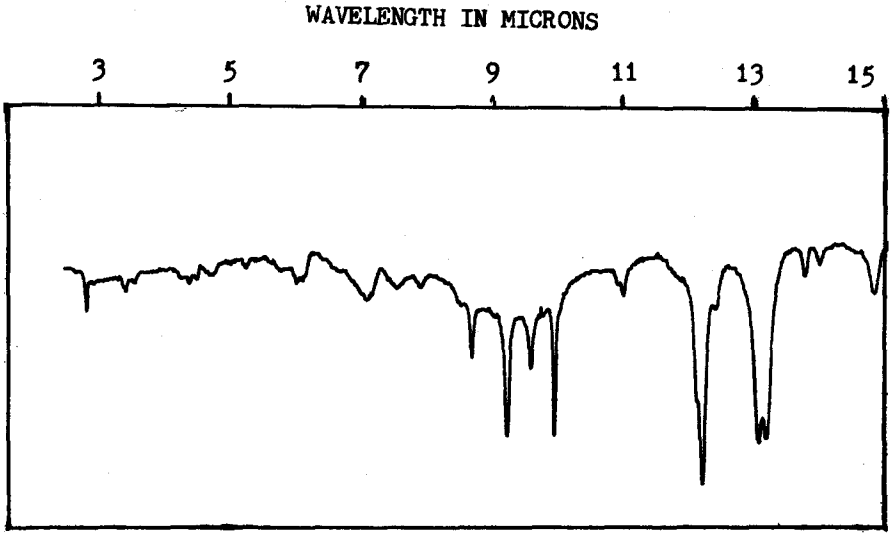

Fig. 4. Infra-red spectra of peak B collected from the Varian Autoprep Model 700-A GLC. 5 mm pathlength in CS_2.

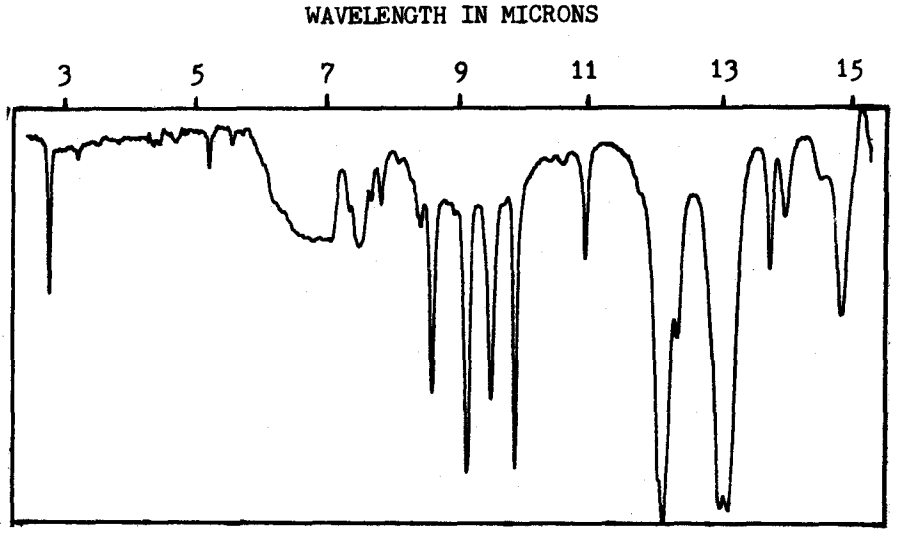

Fig. 5. Infra-red spectra of pure p,p'-kelthane. 1 mm pathlength in CS_2.

benzophenone. The last peak, with a retention time of 16.6 minutes, is p,p'-Kelthane. Both columns were packed with the same material, and the relative retention times on both instruments were identical.

Another chromatogram of interest is shown in Figure 7. This was made by injecting 1 nanogram of p,p'-Kelthane into a Jarrell-Ash electron capture GLC, using Nitrogen carrier gas. The breakdown of p,p'-Kelthane was similar when Nitrogen was used as the carrier gas. The differences in the peak heights of the intermediate breakdown products is probably due to the sensitivities of the two detectors.

Table 1 gives the relative retention times of p,p'-dichlorobenzophenone and p,p'-Kelthane on three commonly used GLC columns. The columns were packed with the same solid support.

TABLE 1

	Time relative to aldrin		
Compound	Dow 11	DC 200	QF 1 + DC 200
Aldrin	1.0	1.0	1.0
p,p'-dichlorobenzophenone	1.0	1.0	1.2
p,p'-DDT	2.9	3.0	3.2
p,p'-Kelthane	3.8	4.6	4.8

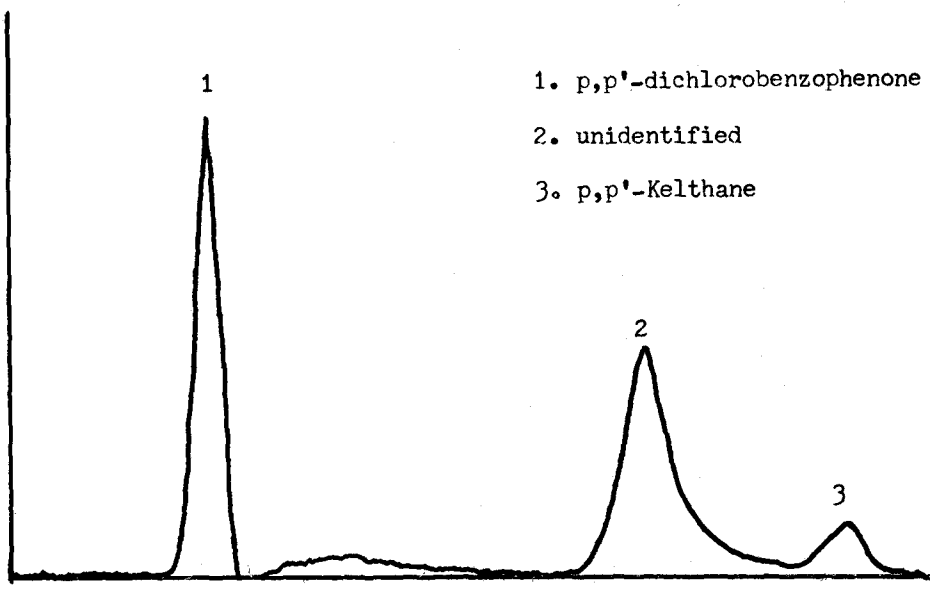

Fig. 6 Chromatogram of 5 micrograms of p,p'-Kelthane injected into a Dohrmann Model 100 GLC with a $\frac{1}{4}$"by 5' glass column packed with 5% Dow 11, 60/80 mesh, DMCS treated Chromosorb W. Inj. Temp. 240°C.,Col. Temp. 218°C. Flow rate 100 ml/min. N_2.

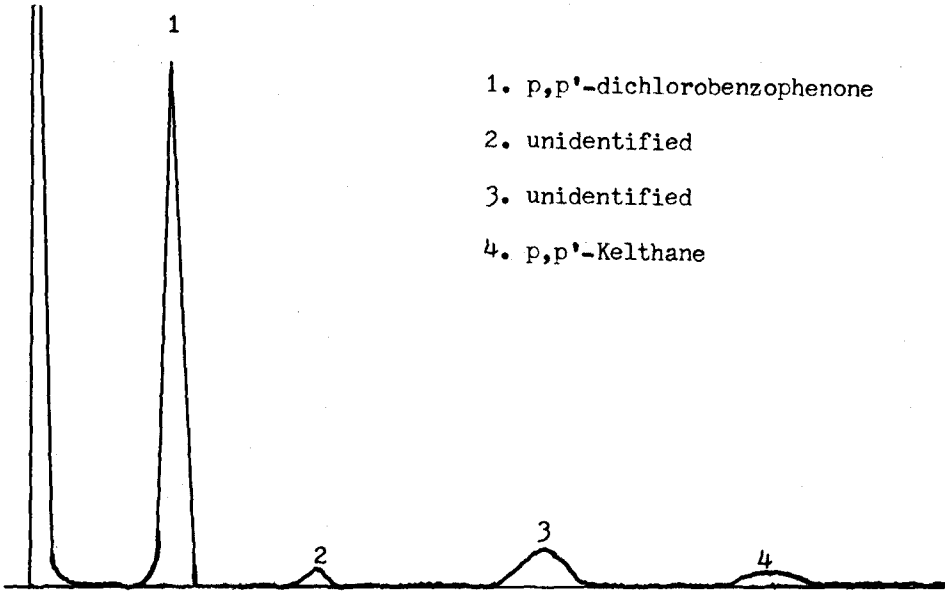

Fig. 7. Chromatogram of 1 nanogram of p,p'-Kelthane injected into a Jarrell-Ash electron capture GLC with a $\frac{1}{4}$" by 5' glass column packed with 10% DC 200, 60/80 mesh Gas-Chrom Q. Inj. Temp. 220°C., Col. Temp. 190°C. Flow rate 250 ml/min. N_2.

Acknowledgements

The assistance and cooperation of Mr. Fred DeLano and Mr. Gordon Roth, California Department of Agriculture, State of California, for their processing of the samples on infrared is greatly appreciated.

References

1 - Burke, J., and Holswade, W., U.S. Department of Health, Education, and Welfare, FDA, Pesticide Analytical Manual Vol. I chlorinated 2.32(E) 12-1-65.

2 - Burke, J., and Giuffrida, L., ibid 7-1-65.

3 - Gudzinowicz, B., The Analysis of Pesticides, Herbicides and Related Compounds. Jarrell-Ash Co., 97 June, 1965.

4 - Westlake, W. E., et. al. This Bulletin, Vol. I, 29 (1966)