

High Temperature Plastic Deformation and Self-Diffusion in Single Crystals of Aromatic Hydrocarbons

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The temperature dependence of self-diffusion in biphenyl and the stress and temperature dependence of steady state plastic deformation (creep) in naphthalene and biphenyl have been studied at temperatures greater than 0.80 times the absolute melting temperature, and under stresses of 0.1 to 0.2 MN m⁻². The results indicate that under these conditions the solids deform by a dislocation climb mechanism. The activation energies for creep are in good agreement with those for self-diffusion. Dislocation concentrations evaluated on the basis of the Weertman analysis of the dislocation climb process are similar to those derived from direct etch-pit counts. These crystals are approximately ten times less plastic than the rotator-phase organic crystals under similar conditions.

1. Introduction

Radiotracer studies of self-diffusion in single crystals of aromatic hydrocarbons have yielded widely varying results [1-4]. One possible cause of this variation is that rapid diffusion along the line defects in the crystal can lead to an enhancement of the tracer diffusion. This results in the evaluation of higher lattice self-diffusion coefficients and lower activation energies for self-diffusion than the true values. Obviously the values obtained will be strongly dependent on the line defect structure of the specimens used. An assessment of the concentration of these defects in the crystal [5] and the measurement of the rates of self-diffusion along these defects [4] have led to the conclusion that the more recently published data [2] are reliable. In order to confirm this, some independent method for measuring self-diffusion in these compounds is required. Studies of the plastic deformation (creep) of metals [6] and rotator-phase* organic solids [7, 8] at temperatures approaching their melting points have shown that this process occurs by a dislocation climb mechanism [9]. Since the rate of climb is limited by the diffusion of lattice vacancies to the dislocation edge, the activation energy for the creep process should be equal to that for self-diffusion [9]. Good agreement has

been found for both of the classes of solid mentioned above. The existence of a similar equality for the aromatic hydrocarbons could confirm the reliability of the radiotracer values. We report the results of a comparison of high temperature creep and self-diffusion in single crystals of the aromatic hydrocarbons naphthalene C₁₀H₈ and biphenyl C₁₂H₁₀.

2. Experimental

2.1. Specimen Preparation

Biphenyl (Fluka, Purum grade) and naphthalene (British Drug Houses, for molecular weight determinations) were further purified by recrystallisation, vacuum-sublimation and zone-refining [10]. The final impurity content was determined by spectroscopic and gas-chromatographic techniques to be less than 10 ppm. Large single crystals were grown from this material by the Bridgman technique. Owing to further refinement during growth the final total impurity content of the crystals was about 1 ppm. After slow cooling, suitable specimens for the diffusion and plastic flow experiments were cut from the crystals. Only then was the final annealing, to reduce thermal and stress-induced defects, carried out. Microscopic examination indicated that the concentration of gross boundary

*These materials are the high temperature cubic phases of solids which comprise globular molecules. The molecules in these phases have considerable rotational freedom and the solids exhibit a remarkably high plasticity compared to that of the more brittle solids described here. In extreme cases, they flow readily under gravity.

structure was small and varied little from crystal to crystal. Dislocation etching studies [5, 11] revealed that the "as-grown" crystals contained about 10^6 to 10^7 dislocations per cm^{-2} . This could be reduced by prolonged annealing, as shown in table I. Longer periods than those quoted yielded no further reduction.

TABLE I The effect of annealing at 340°K on the dislocation content in biphenyl crystals

Annealing time (hours)	Dislocation content (cm^{-2})
0 (as-grown)	10^6 to 10^7
240	10^5 to 10^6
480	10^4 to 10^5

2.2. Diffusion Experiments

The self-diffusion studies on biphenyl were carried out perpendicular to the *ab*, (001) plane. Biphenyl-1- ^{14}C , prepared by the reaction of Gardner *et al* [12] from bromobenzene-1- ^{14}C (0.1 mc/8.58 mg) (Radiochemical Centre, Amersham), was used as the radioactive tracer. Deposition of the tracer on the surface of the crystal was effected by evaporation *in vacuo* or by deposition from benzene solution. The crystals were annealed at temperatures between 323 and 341°K and for periods of 65 to 220 h. Following the diffusion anneal, the sectioning method, as described for naphthalene by Sherwood and White [2], was used to determine the diffusion profile through the crystal. From this the diffusion coefficient can be calculated. Measurements were made with crystals of equivalent purity as a function of pre-annealing period.

2.3. Plastic Deformation Experiments

Because of the difficulty of clamping biphenyl and naphthalene for tension tests, the plastic flow studies on these materials were carried out in compression. The crystals were compressed perpendicular to the *ab*, (001) plane. Compression tests were made using a standard tensile test machine incorporating a specially designed compression cage complete with strict temperature control facilities ($\pm 0.1^\circ\text{K}$). The temperature-dependence and the stress-dependence of creep were obtained by measuring the variation of the deformation rate with temperature at constant stress and with stress at constant temperature respectively, using the change technique [7]. Changes in temperature and stress were carried out as quickly as possible. The

experimental curves showed well defined primary and secondary creep regions [6]. Each deformation increment was followed for a sufficient period of time to ensure that measurements were made in the linear region, i.e. at constant deformation rate, of the creep curves. The total deformation was kept within 10% of the total strain in a complete experiment in order to minimise errors due to barrelling and stress variation. The applied stresses used were in the range 0.1 to 0.2 MN m^{-2} , and the temperature ranges 308 to 338°K for biphenyl (melting point 343°K) and 308 to 348°K for naphthalene (melting point 353°K). The strain rates produced were about 10^{-5} sec^{-1} . Only well annealed crystals were used in these experiments. Because of the limitation of each experiment to 10% total strain, only a few (4 to 5) stress or temperature changes could be made on each crystal. The results quoted below refer to the average of values obtained from the examination of a number of crystals.

3. Results

3.1. Diffusion

For diffusion from an infinitely thin source into a semi-infinite solid, integration of Fick's law gives an equation

$$C_{(x,t)} = Q/(\pi Dt)^{1/2} \exp(-x^2/4Dt) \quad (1)$$

where $C_{(x,t)}$ is the concentration of the diffusing species at distance x into the crystal after time t , Q the total quantity of diffusing species deposited on the surface of the specimen at $t = 0$ and D the diffusion coefficient. All crystals studied yielded linear experimental plots of the logarithmic form of equation 1. Within the experimental error, the diffusion coefficients for crystals subjected to a particular pre-annealing treatment were found to vary with temperature according to an equation

$$D = D_0 \exp(-E_t/RT) \quad (2)$$

where D_0 is a constant and E_t the activation energy of the process. The results of the experiments are summarised in figs. 1 and 2 and in tables II and III. The general trend in the data

TABLE II Self-diffusion coefficients in pure biphenyl

Temperature $T^\circ\text{C}$	$1/T$ ($^\circ\text{K}^{-1} \times 10^{-3}$)	Diffusion coefficient, D ($\text{cm}^2\text{ sec}^{-1}$)
66.2	2.946	3.23×10^{-12}
62.9	2.976	1.75×10^{-12}
60.5	2.997	1.16×10^{-12}
58.7	3.013	8.13×10^{-13}

TABLE III Self-diffusion parameters for biphenyl

Crystal	Pre-annealing period* (hours)	$\log D_0$	E (kcal mole ⁻¹)
A	24	12.6 ± 1.0	36.1 ± 1.4
B	240	13.0 ± 1.0	37.5 ± 4.4
C	480	14.4 ± 1.0	40.1 ± 2.5

*at 340° K (melting point 343° K)

is that prolonged pre-annealing of the crystals leads to lower measured diffusion coefficients. There would therefore appear to be an enhancement of diffusion due to the presence of greater numbers of extrinsic defects at the shorter anneal times.

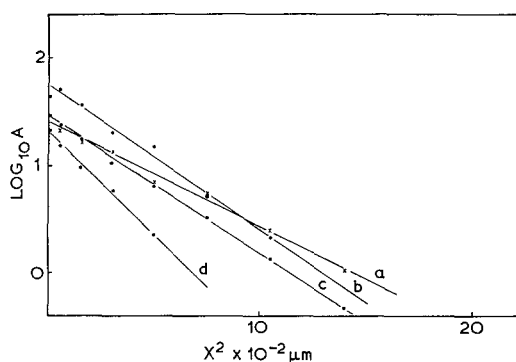


Figure 1 Diffusion profiles plotted as $\log_{10} A$ (counts $\text{sec}^{-1} \text{mg}^{-1}$) versus x^2 for the specially well annealed crystal of biphenyl.

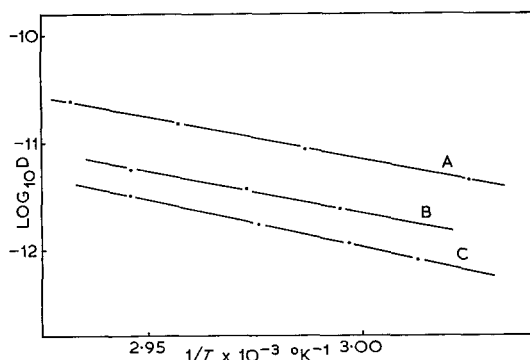


Figure 2 Logarithmic plot of the equation $D = D_0 \exp(-E/RT)$ for the biphenyl crystals.

3.2. Plastic Flow

The strain rate at constant temperature, $\dot{\epsilon}(T)$, is empirically related to the stress σ by the expression [13, 14]:

$$\dot{\epsilon}(T) = a \exp(m\sigma) + b\sigma^n \quad (3)$$

where a , b , m and n are constants.

At low stresses this expression reduces to the power law

$$\dot{\epsilon}(T) = b\sigma^n \quad (4)$$

Some typical experimental plots of the stress-dependence of the strain-rate of the crystals are shown in fig. 3 and the average values for the stress exponent, n , are given in table IV.

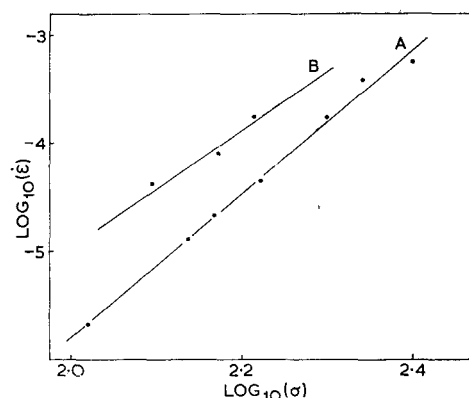


Figure 3 Logarithmic plots of the stress dependence σ (kN m^{-2}) of the strain rate $\dot{\epsilon}$ (sec^{-1}) for (A) naphthalene and (B) biphenyl.

TABLE IV Comparison of results for biphenyl and naphthalene

	Biphenyl	Naphthalene
Stress exponent, n	5.1	5.3
A.E. for creep, E_c (kcal mole ⁻¹)	33.6 ± 3.6	31.3 ± 3.4
A.E. for diffusion, E_t (kcal mole ⁻¹)	40.1 ± 2.5	42.7 ± 1.6
A.E. for sublimation (kcal mole ⁻¹)	17.7	17.9
$\log(D_0 \text{ cm}^2 \text{ sec}^{-1})$	14.4	15.4
Observed dislocation density (cm^{-2})	$10^4 - 10^5$	$10^3 - 10^4$
Calculated dislocation density (cm^{-2})	0.9×10^5	1.1×10^5

The dependence of the strain-rate on the temperature can be expressed by an Arrhenius relationship [13, 14]

$$\dot{\epsilon}(\sigma) = \exp(-E(\sigma)/RT) \quad (5)$$

At high temperature, creep is usually diffusion controlled. Either vacancy migration across the crystal grains (Nabarro-Herring Creep [15, 16]) or dislocation climb [9] is the most likely rate-controlling mechanism. Theory indicates that

these mechanisms are characterised by a stress exponent equal to unity and 4.5 respectively. Experimental studies of the latter mechanism yield values of n in the range 4 to 6 [9]. It would appear from the values of n found here (table IV) that a dislocation climb process is in operation. For this mechanism, Weertman [9] has proposed that the creep rate is given by the expression

$$\dot{\epsilon} = (A\sigma^n/kT) \exp(-E_c/RT) \quad (6)$$

where A is a constant, $n = 4.5$, and E_c is the activation energy for creep which should equal E_t , the activation energy for self-diffusion. E_c can thus be evaluated from the slope of plots of $\log \dot{\epsilon}T$ versus $1/T$.

Some typical experimental results are shown in fig. 4. Average values of E_c are quoted in table IV.

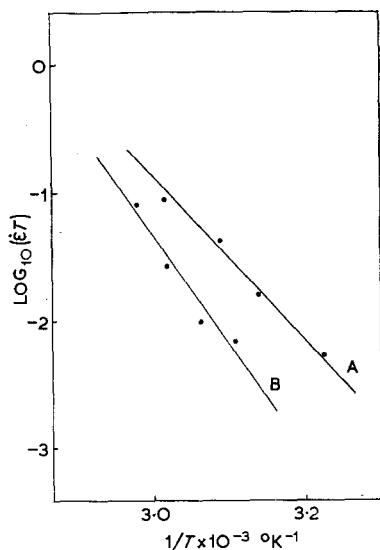


Figure 4 Typical plots of the temperature dependence of the strain rate $\dot{\epsilon}$ (sec^{-1}) for (A) naphthalene and (B) biphenyl.

4. Discussion

4.1. Dislocation Enhancement of Lattice Self-Diffusion Coefficients

The variation of the self-diffusion coefficients reflects the length of the crystal pre-annealing period and presumably can be ascribed to diffusion enhancement due to the presence of an excess of strain- and thermally-induced defects in the crystals.

In these solids, diffusion along these line defects is considerably faster than through the lattice [4]. One would therefore expect an

enhancement of self-diffusion even at low line defect concentrations. Where this effect is significant, i.e. where there are gross line defects present, the experimental plots of the logarithmic form of equation 1 are curved and not linear as expected [2]. In the present case, all such plots were linear over the full measurable range, indicating a unique diffusion coefficient which presumably should represent lattice self-diffusion. Hart [17] has shown, however, that where the density of dislocations, etc. is such that the average grain size or inter-dislocation distance $a_g < (Dt)^{1/2}$, the tracer molecule will be near a line defect for a considerable part of its diffusing lifetime. As a consequence it will be subjected to an enhanced diffusion coefficient compounded from the true lattice coefficient, D_l , and that for boundary diffusion, D_g , as follows

$$D = fD_g + (1 - f)D_l \quad (7)$$

f is the fraction of the diffusing species present in the various line defects. Thus a linear diffusion plot ($\ln A$ versus x^2) is not definite proof that no enhancement exists. We conclude that it is for this reason that we find a variation of D and hence D_0 and E_t with pre-annealing period.

Some estimate can be made of the degree of enhancement in the various crystals. For low values of f equation 7 reduces to

$$D/D_l = f \times D_g/D_l + 1 \quad (8)$$

If we assume that the measured dislocation counts are indicative of the total line defect concentration in the crystals and that each dislocation core involves ten molecules, then we evaluate that $f = 10^5$ dislocations/ $\text{cm}^2 \times 10^{-15}$ $\text{cm}^2/\text{molecule} \times 10$ molecules/dislocation, i.e. $f < 10^{-9}$ for the best crystals (C, table III) and 10^{-8} and 10^{-7} respectively for the crystals B and A. Furthermore, if we assume that we can detect an enhancement of 1%, then from equation 8 we see that enhancement will become marked in each of the three cases when $D_g/D_l > 10^5$ (A), 10^6 (B) and 10^7 (C). No measurements of grain-boundary self-diffusion have been made for biphenyl, however, the structural similarity between this solid and the related solids anthracene and naphthalene and the more particular similarity of the self-diffusion data for the three solids [2, 18] suggest that a similar correspondence will exist for grain-boundary self-diffusion. For these other solids $D_g/D_l \approx 10^6$ at the melting point [4, 18]. Thus we can only anticipate that we shall see true lattice self-diffusion for the

well annealed crystal and then only at temperatures greater than $0.95 T_m$ (melting temperature). Since this corresponds to a temperature of $1/T = 0.00310 \text{ k}^{-1}$ then we see that the best data probably do represent true lattice self-diffusion. This being so, then using the same arguments as for naphthalene [2], it seems likely that this represents diffusion by a vacancy mechanism.

4.2. Correlation between Creep and Self-Diffusion

The present self-diffusion results are similar to those obtained in this laboratory for other organic solids in that the activation energy for self-diffusion is approximately double the latent heat of sublimation of the solid [18]. Other experiments on aromatic solids [3], sulphur [19] and α -white phosphorus [20] have yielded values which are approximately equal to the sublimation energy. The present study provides some confirmation of the former equivalence.

Experimental studies on metals and ceramic systems have shown an approximate 1:1 correspondence between the activation energies for self-diffusion and for high-temperature creep. The correlation between the two sets of data for biphenyl and naphthalene is shown in table IV. A further comparison with the previous data for metals and plastic organic crystals is shown in fig. 5. From the figure it will be seen that, on average, E_t is slightly greater than E_c and that the latter probably represents a minimum value for self-diffusion. Thus, it seems possible that, within the experimental error, high-temperature creep in these solids is self-diffusion controlled and hence the activation energy is much greater than the latent heat of sublimation of the solid. The low values obtained in some previous studies probably resulted from diffusion enhancement in the crystals used.

4.3. Correlation between Calculated and Observed Dislocation Densities

Although a comparison of activation energies alone is insufficient evidence on which to base a firm conclusion that the creep process under consideration is self-diffusion controlled, the magnitude of the stress exponent and its similarity to the theoretical value [9] and to the experimental range of values for previous studies of dislocation-climb creep [9] do add some weight to this conclusion. Further confirmation can however be obtained by a comparison of the actual strain rates with those predicted by theory

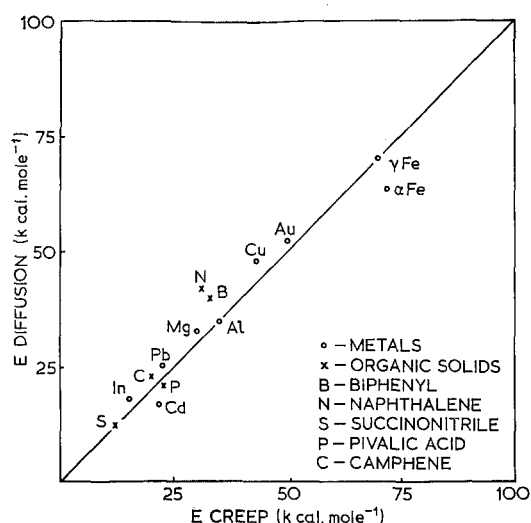


Figure 5 Comparison of the activation energies of diffusion and creep for metals and organic solids.

or alternatively, since the theoretical evaluation requires the knowledge of the dislocation density of the specimen, by comparing the actual dislocation density with that evaluated on the basis that the process is occurring by dislocation climb.

Weertman [9] has shown that for the dislocation climb process, the strain rate should be related to the number of dislocation sources by the expression

$$\dot{\epsilon} = \frac{3\sqrt{6}\pi^2\sigma^4 \cdot 5D}{2^5(bM)^{0.5}\mu^{3.5}kT} \quad (9)$$

where b is the length of the Burgers vector, estimated as 1×10^{-7} cm, this being the approximate intermolecular distance. μ is the shear modulus and is estimated at 4×10^{10} dynes/cm². M is the number of Frank-Read sources in one slip system and is related to the dislocation density N [9] by

$$N = (1.9M^{0.5})^{4/3} \quad (10)$$

Using White's data for naphthalene and the present data for the well-annealed crystals, calculated dislocation densities can be obtained. These are compared with the etching studies in table IV. It can be seen that the agreement is reasonable within the usual error involved in etch-pit counting. The observed dislocation counts refer to non-basal dislocations, but it is known from other studies that dislocations do form and move on other crystallographic planes

and it seems reasonable to assume that the densities of these will be similar.

5. Conclusions

We conclude that at high temperatures and under conditions of low stress, the plastic deformation of aromatic hydrocarbon single crystals occurs by a dislocation climb mechanism.

The stresses required to produce a strain rate of about 10^{-5} sec⁻¹ in these materials are approximately ten times greater than for the rotator-phase organic crystals under similar temperature conditions. This observation is in agreement with previous qualitative observations [21].

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References

1. J. N. SHERWOOD and S. J. THOMSON, *Trans. Faraday Soc.* **56** (1960) 4413.
2. J. N. SHERWOOD and D. J. WHITE, *Phil. Mag.* **15** (1967) 745.
3. P. J. REUCROFT, H. K. KEVORKIAN, and M. M. LABES, *J. Chem. Phys.* **44** (1966) 4416; C. H. LEE, H. K. KEVORKIAN, P. J. REUCROFT, and M. M. LABES, *ibid* **42** (1965) 1406.
4. J. N. SHERWOOD and D. J. WHITE, *Phil. Mag.* **16** (1967) 975.
5. N. T. CORKE, A. A. KAWADA, and J. N. SHERWOOD, *Nature* **213** (1967) 62.
6. A. J. KENNEDY, "Processes of creep and fatigue in metals" (Oliver and Boyd, Edinburgh 1962).
7. H. M. HAWTHORNE and J. N. SHERWOOD, *Trans. Faraday Soc.* **66** (1970) 1783, 1792, 1799.
8. N. T. CORKE, H. A. RESING, and J. N. SHERWOOD, *Phys. Rev. Letters* **20** (1968) 1227(c).
9. J. WEERTMAN, *J. Appl. Phys.* **28** (1957) 362.
10. J. N. SHERWOOD, "Purification of Inorganic and Organic Materials", Ed. M. Zief (M. Dekker, New York, 1969).
11. N. T. CORKE, B. S. SHAH, and J. N. SHERWOOD, to be published.
12. J. H. GARDNER and P. BORGSTROM, *J. Amer. Chem. Soc.* **51** (1929) 3375.
13. J. E. DORN, *J. Mech. Phys. Solids* **3** (1955) 85.
14. *Idem*, "Creep and recovery" (ASM, Metals Park, Ohio 1957).
15. F. R. N. NABARRO, *Report Conf. on Strength of Materials Phys. Soc.*, London (1947).
16. C. HERRING, *J. Appl. Phys.* **21** (1950) 437.
17. E. W. HART, *Acta Metallurgica* **5** (1967) 597.
18. J. N. SHERWOOD, *Mol. Cryst. & Liq. Cryst.* **9** (1969) 37.
19. R. G. CUDDEBACK and H. G. DRICKAMER, *J. Chem. Phys.* **19** (1951) 790.
20. N. H. NACHTRIEB and G. HANDLER, *ibid* **23** (1955) 1187.
21. A. MICHELS, *Bull. Soc. Chem.* **57** (1948) 575.

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